

(19)



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(11)

EP 0 887 700 A1

J1017 U.S. PTO
10/042261
01/11/02

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

30.12.1998 Bulletin 1998/53

(51) Int. Cl.⁶: G03C 1/12

(21) Application number: 98201969.7

(22) Date of filing: 12.06.1998

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 24.06.1997 US 881777

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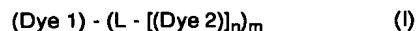
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(54) Sensitizing dyes for enhanced light absorption

(57) A silver halide photographic element comprises at least one silver halide emulsion spectrally sensitized by a molecule of formula I:



wherein Dye 1 comprises a first chromophore and Dye 2 comprises a second chromophore, wherein Dye 1 adsorbs to silver halide more strongly than Dye 2, and Dye 1 absorbs light at a longer wavelength than Dye 2, L is an organic linking group containing at least one hetero atom which is not part of an amide or ester group, and m and n are independently an integer of 1-3.

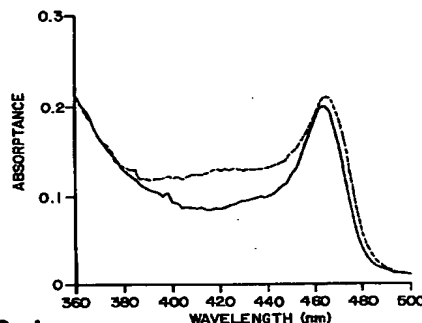


FIG. 1a

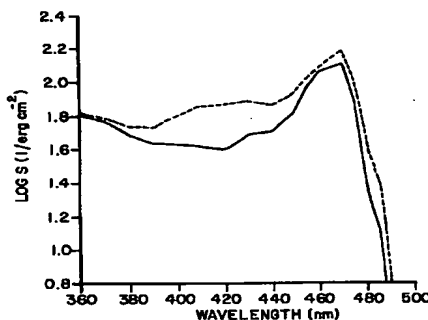


FIG. 1b

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Description

FIELD OF THE INVENTION

5 This invention relates to a silver halide photographic element containing at least one silver halide emulsion which has associated with it at least one sensitizing dye which contains two or more chromophores.

BACKGROUND OF THE INVENTION

10 J-aggregating cyanine dyes are used in many photographic systems. It is believed that these dyes adsorb to a silver halide emulsion and pack together on their "edge" which allows the maximum number of dye molecules to be placed on the surface. However, a monolayer of dye, even one with as high an extinction coefficient as a J-aggregated cyanine dye, absorbs only a small fraction of the light impinging on it per unit area. The advent of tabular emulsions allowed more dye to be put on the grains due to increased surface area. However, in most photographic systems, it is still the case that not all the available light is being collected.

One way to achieve greater light absorption is to increase the amount of spectral sensitizing dye associated with the individual grains beyond monolayer coverage of dye (some proposed approaches are described in the literature, G. R. Bird, *Photogr. Sci. Eng.*, 18, 562 (1974)). The need is especially great in the blue spectral region where a combination of low source intensity and relatively low dye extinction result in a deficient photoresponse.

20 One approach is to synthesize molecules in which two dye chromophores are covalently connected by a linking group. These types of dye molecules will be referred to as binary dyes. US 3,622,317 describes examples of cyanine dyes connected together by an aliphatic chain. US 3,976,493 describes the formation of binary dyes from bis-quaternary salts. The bis-quaternary salts, and consequently the binary dyes prepared from them, are connected by an amide-containing linking group. US 3,976,493 describes several examples of two cyanine dyes connected together as well as one example of a merocyanine dye containing a thiobarbituric acid nucleus connected to a cyanine dye. US 3,976,640 describes a process for the preparation of binary dyes from bis-quaternary salts. Several examples of cyanine dyes connected together are given. EP 565,074 describes a process for forming binary dyes. Binary dye examples are cyanine dyes connected to either merocyanine or coumarin chromophores. Kokai Sho 64(1989)91134 describes binary dyes in which one dye is adsorbed to silver halide and the second dye must meet a number of requirements. For example, the second dye must have not less than two sulfo and/or carboxy groups included as substituents.

PROBLEM TO BE SOLVED BY THE INVENTION

35 Not all the available light is being collected in most photographic systems. The binary dye approaches described previously suffer from the fact that when the two dyes are connected they can interfere with each others performance, e.g. not aggregating on or adsorbing to the silver halide grain properly.

SUMMARY OF THE INVENTION

40 We have found that by using sensitizing dyes having two chromophores connected by a linking group which contains at least one hetero atom (formula I) we can increase light collection and photographic sensitivity (speed). We can also obtain a broader sensitization envelope and decrease illuminance sensitivity in photographic elements which leads to better color reproduction.

45 One aspect of this invention comprises a silver halide photographic element comprising at least one silver halide emulsion spectrally sensitized by a molecule of formula I:



50 wherein Dye 1 comprises a first chromophore and Dye 2 comprises a second chromophore, wherein Dye 1 adsorbs to silver halide more strongly than Dye 2, and Dye 1 absorbs light at a longer wavelength than Dye 2, L is an organic linking group containing at least one hetero atom which is not part of an amide or ester group, and m and n are independently an integer of 1-3.

In a preferred embodiment of the invention, Dye 2 is a merocyanine dye which in a more preferred embodiment contains an acidic substituent. In another preferred embodiment of the invention, Dye 1 is a cyanine dye. In yet another preferred embodiment of the invention, the organic linking group also contains an amide group.

ADVANTAGEOUS EFFECT OF THE INVENTION

This sensitizing dye of formula I provides enhanced speed and/or better color reproduction and/or improved illuminant sensitivity compared to sensitizing the emulsion using (Dye 1) and (Dye 2) as separate sensitizing dyes or sensitizing the emulsion with a binary dye of the prior art.

BRIEF DESCRIPTION OF THE DRAWING

Figs. 1a and 1b show the light absorption profile and spectral sensitivity of Dye 1-1 of the invention compared to comparative Dye C-1, as discussed more fully below.

DETAILED DESCRIPTION OF THE INVENTION

In the dye of formula I, Dye 1 is strongly to moderately adsorbed to the silver halide grain. Preferably, Dye 2 is not adsorbed or only weakly adsorbed to the silver halide grain. The relative adsorption strengths of Dye 1 and Dye 2 can be determined by using model dyes and well-known techniques for measuring adsorption strength. Useful analogs of Dye 1 and Dye 2 can be obtained by replacing the linking group (L) with an acidic substituent such as a sulfonic or carboxylic acid. For example, ((Dye 1)-SG) and ((Dye 2)-SG), where SG is a solubilizing group such as: $-(CH_2)_3SO_3^-$ or $-(CH_2)_2CO_2^-$ can be prepared. The dye adsorption strength (K) and the area each dye molecule occupies on the silver halide surface can be determined by well-known techniques in a silver halide system (for example see W. West B. H. Carroll, and D. H. Whitcomb, J. Phys. Chem, 56, 1054 (1962)). Preferably, the emulsion used to determine the adsorption strength should be as close as possible to the emulsion of practical interest.

In a preferred embodiment, the adsorption strength of ((Dye 2)-SG) is less than 30% that of ((Dye 1)-SG), more preferably the adsorption strength of ((Dye 2)-SG) is less than 10% that of ((Dye 1)-SG), more preferably the adsorption strength of ((Dye 2)-SG) is less than 5% that of ((Dye 1)-SG), more preferably the adsorption strength of ((Dye 2)-SG) is zero or close to zero.

In a similar fashion, it is preferred that the area each molecule of the invention dye, (Dye 1) - [L - (Dye 2)_n]_m, occupies is no more than 150% of the area of the corresponding model dye, ((Dye 1)-SG) on the silver halide emulsion. More preferably the invention dye should take no more than 125% of the area of the corresponding ((Dye 1)-SG) model dye. More preferably the invention dyes should occupy no more than 110% of the area of the corresponding model dye. Most preferably the invention dyes should occupy approximately the same or less area on the silver halide emulsion as the corresponding model dye ((Dye 1)-SG).

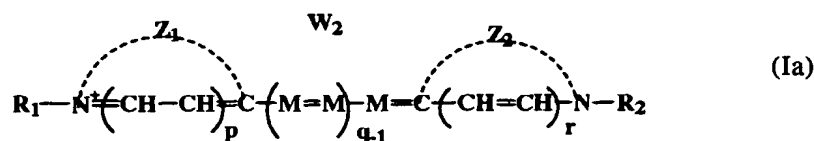
In formula I, Dye 1 and Dye 2 are light-absorbing molecules (chromophores) that adsorb light preferably in the visible wavelength of the spectrum. Dye 2 acts like an antenna dye and absorbs light and transfers that energy to Dye 1 for example by a Förster-type energy transfer mechanism (see Th. Förster, Discuss. Faraday Soc., 27, 7, 1959). The extinction coefficient of Dye 1 and Dye 2 should be high. It is useful to use the extinction coefficients of the model dyes, ((Dye 1)-SG) and ((Dye 2)-SG), at their wavelengths of maximum light absorption to determine their light absorbing properties. Preferably, the extinction coefficient of the model dyes, measured in a solvent such as methanol, should be at least $1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$. More preferably their extinction coefficients should be at least $3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.

For the inventive dye of formula I, to effect energy transfer from Dye 2 to Dye 1, the excitation energy of Dye 1 should be less, or of longer absorption wavelength, than the excitation energy of Dye 2 when the inventive dye of formula I is incorporated into a photographic element containing silver halide emulsion.

In a preferred embodiment of the invention, the dye of formula I has a net charge of -1.

Dye 1 is preferably a cyanine dye, merocyanine dye, complex cyanine dye, complex merocyanine dye, homopolar cyanine dye, or hemicyanine dye, etc.. Of these dyes, merocyanine dyes containing a group that adsorbs to silver halide, such as a thiocarbonyl group and cyanine dyes are particularly useful. Of these cyanine dyes are especially useful.

Particularly preferred as Dye 1 is a cyanine dye having structure Ia or a merocyanine dye having structure Ib;



wherein:

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Z_1 and Z_2 may be the same or different and represent the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus (see T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977 for a definition of basic and acidic nucleus),

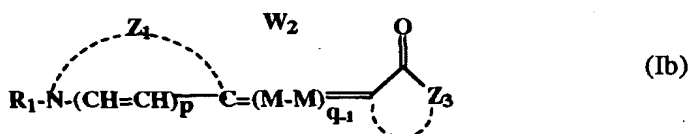
each M independently represents a substituted or unsubstituted methine group,

q is a positive integer of from 1 to 4,

p and r each independently represents 0 or 1,

R_1 and R_2 each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl, and

W_2 is a counterion as necessary to balance the charge;



wherein:

Z_1 , R_1 , M, p , q and W_2 are as defined above for formula (Ia) and

Z_3 represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus, which preferably contains a group that adsorbs to silver halide, e.g., a thiocarbonyl group.

Especially preferred as Dye 1, are cyanine dyes of the formula Ia where:

q is 1 to 2,

Z_1 and Z_2 represent the atoms necessary to form a substituted or unsubstituted thiazole, oxazole, imidazole, selenazole, or quinoline ring, which may be the same or different,

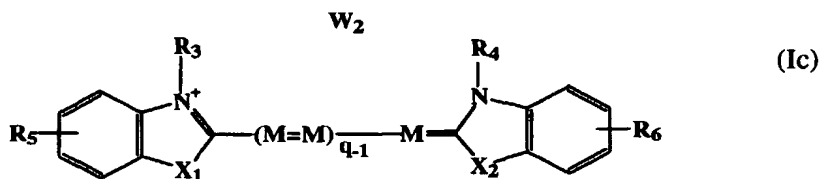
p and r each independently represents 0 or 1,

R_1 and R_2 each independently represents substituted or unsubstituted alkyl.

and

W_2 is a counterion as necessary to balance the charge;

Also especially preferred as Dye 1, are cyanine dyes of the formula Ic:



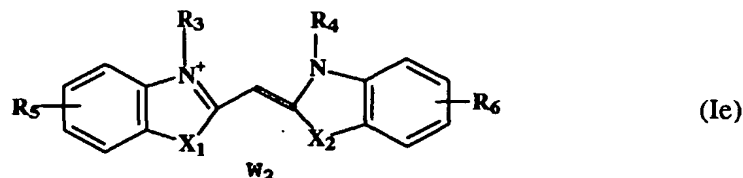
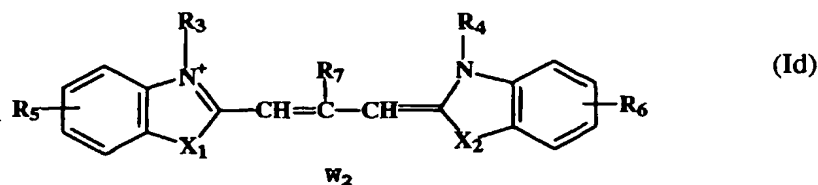
wherein:

q is 1 or 2,

R_3 and R_4 each independently represents substituted or unsubstituted alkyl,

R_5 and R_6 represent one or more substituents including possible fused aromatic rings,

Particularly preferred as Dye 1, are cyanine dyes of the formula Id or Ie:

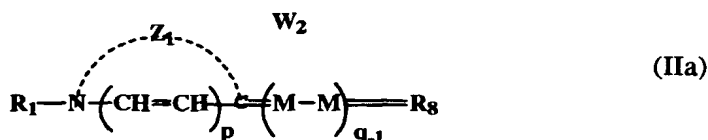


wherein:

25 R_3 and R_4 each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl, R_5 and R_6 represent one or more substituents including possible fused aromatic rings, and R_7 represents hydrogen or substituted or unsubstituted alkyl or substituted or unsubstituted aryl.

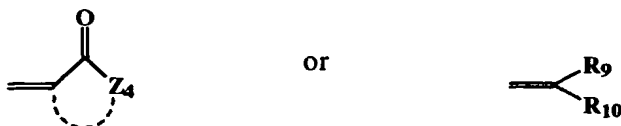
30 Dye 2 is preferably a cyanine dye, merocyanine dye, arylidene dye, complex cyanine dye, complex merocyanine dye, homopolar cyanine dye, hemicyanine dye, styryl dye, hemioxonol dye, oxonol dye, anthraquinone dye, triphenylmethane dye, azo dye type, azomethine dye, coumarin dye or others. Of these dyes, merocyanine dyes, coumarin dyes, arylidene dyes and oxonol dyes are particularly useful. Merocyanine dyes are especially useful. The merocyanine dyes that can be employed preferably contain 5- or 6-membered heterocyclic nuclei such as a barbituric acid nucleus, pyrazolin-5-one nucleus, a benzoylacetone nucleus, or an isoxazolinone nucleus, etc.

Particularly preferred as Dye 2 are dyes of the structure IIa, IIb, IIc, IId, IIe, or IIf:



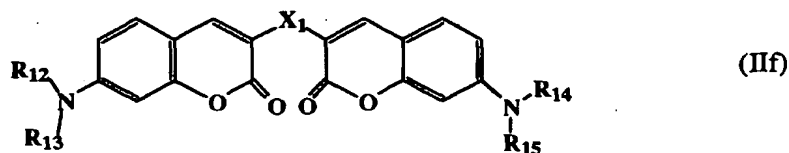
wherein:

45 Z_1 , R_1 , M , p , q and W_2 are as defined above for formula (Ia) and R_8 represents:



55 wherein:

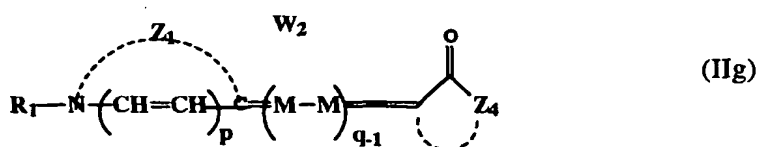
Z_4 represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus which preferably does not contain a group that adsorbs to silver halide, e.g., a thiocarbonyl group, and R_9 and R_{10} each independently represents a cyano group, an ester group, an acyl group, a carbamoyl group or an



10 wherein:

X₁ represents a carbonyl group, sulfonyl group or a substituted nitrogen atom, and
R₁₂ - R₁₅ each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl group.

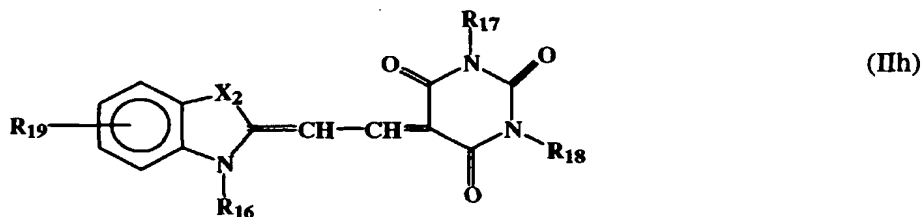
15 Especially preferred as Dye 2 are merocyanine dyes of the formula:



25 wherein:

Z₁, Z₄, R₁, M, p, q and W₂ are as defined above for formula (IIa).

30 Especially preferred as Dye 2 are merocyanine dyes of the structure:



40 wherein:

X₂ is O, S, or Se,

45 R₁₆, R₁₇ and R₁₈ are independently substituted or unsubstituted alkyl or substituted or unsubstituted aryl, and
R₁₉ represents a charged substituent, such as -SO₃⁻ or -N(Me)₃⁺, or a sterically bulky substituent, such as -C(CH₃)₃ or -Si(Me)₃.

50 When reference in this application is made to a substituent "group", this means that the substituent may itself be substituted or unsubstituted (for example "alkyl group" refers to a substituted or unsubstituted alkyl). Generally, unless otherwise specifically stated, substituents on any "groups" referenced herein or where something is stated to be possibly substituted, include the possibility of any groups, whether substituted or unsubstituted, which do not destroy properties necessary for the photographic utility. It will also be understood throughout this application that reference to a compound of a particular general formula includes those compounds of other more specific formula which specific formula falls within the general formula definition. Examples of substituents on any of the mentioned groups can include known substituents, such as: halogen, for example, chloro, fluoro, bromo, iodo; alkoxy, particularly those with 1 to 6 carbon atoms (for example, methoxy, ethoxy); substituted or unsubstituted alkyl, particularly lower alkyl (for example, methyl, trifluoromethyl); alkenyl or thioalkyl (for example, methylthio or ethylthio), particularly either of those with 1 to 6

carbon atoms; substituted and unsubstituted aryl, particularly those having from 6 to 20 carbon atoms (for example, phenyl); and substituted or unsubstituted heteroaryl, particularly those having a 5 or 6-membered ring containing 1 to 3 heteroatoms selected from N, O, or S (for example, pyridyl, thienyl, furyl, pyrrolyl); and others known in the art. Alkyl substituents may specifically include "lower alkyl", that is having from 1 to 6 carbon atoms, for example, methyl or ethyl. Further, with regard to any alkyl group, alkylene group or alkenyl group, it will be understood that these can be branched or unbranched and include ring structures.

For Dye 1, any conventionally utilized nuclei for cyanine dyes are applicable to these dyes as basic heterocyclic nuclei. That is, a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, a pyridine nucleus, etc., and further, nuclei formed by condensing alicyclic hydrocarbon rings with these nuclei and nuclei formed by condensing aromatic hydrocarbon rings with these nuclei, that is, an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, a quinoline nucleus, etc., are appropriate. The carbon atoms of these nuclei can also be substituted.

In the above formulas, Z_1 and Z_2 each independently represents the atoms necessary to complete a substituted or unsubstituted 5- or 6-membered heterocyclic nucleus. These include a substituted or unsubstituted: thiazole nucleus, oxazole nucleus, selenazole nucleus, quinoline nucleus, tellurazole nucleus, pyridine nucleus, thiazoline nucleus, indoline nucleus, oxadiazole nucleus, thiadiazole nucleus, or imidazole nucleus. This nucleus may be substituted with known substituents, such as halogen (e.g., chloro, fluoro, bromo), alkoxy (e.g., methoxy, ethoxy), substituted or unsubstituted alkyl (e.g., methyl, trifluoromethyl), substituted or unsubstituted aryl, substituted or unsubstituted aralkyl, sulfonate, and others known in the art.

In one embodiment of the invention, Z_1 and Z_2 each independently represent the atoms necessary to complete a substituted or unsubstituted thiazole nucleus, a substituted or unsubstituted selenazole nucleus, a substituted or unsubstituted imidazole nucleus, or a substituted or unsubstituted oxazole nucleus.

Examples of useful nuclei for Z_1 and Z_2 include: a thiazole nucleus, e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 5-phenylbenzothiazole, 6-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylbenzothiazole, 5-hydroxybenzothiazole, 6-5-hydroxybenzothiazole, naphtho[2,1-d]thiazole, 5-ethoxynaphtho[2,3-d]thiazole, 8-methoxynaphtho[2,3-d]thiazole, 7-methoxynaphtho[2,3-d]thiazole, 4'-methoxythianaphtho-7', 6'-4,5-thiazole, etc.; an oxazole nucleus, e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, naphtho[2,1-d]oxazole, naphtho[1,2-d]oxazole, etc.; a selenazole nucleus, e.g., 4-methylselenazole, 4-phenylselenazole, benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, naphtho[2,1-d]selenazole, naphtho[1,2-d]selenazole, etc.; a pyridine nucleus, e.g., 2-pyridine, 5-methyl-2-pyridine, 4-pyridine, 3-methyl-4-pyridine, 3-methyl-4-pyridine, etc.; a quinoline nucleus, e.g., 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, etc.; a tellurazole nucleus, e.g., benzotellurazole, naphtho[1,2-d]benzotellurazole, 5,6-dimethoxybenzotellurazole, 5-methoxybenzotellurazole, 5-methylbenzotellurazole; a thiazoline nucleus, e.g., thiazoline, 4-methylthiazoline, etc.; a benzimidazole nucleus, e.g., benzimidazole, 5-trifluoromethylbenzimidazole, 5,6-dichlorobenzimidazole; and indole nucleus, 3,3-dimethylindole, 3,3-diethylindole, 3,3,5-trimethylindole; or a diazole nucleus, e.g., 5-phenyl-1,3,4-oxadiazole, 5-methyl-1,3,4-thiadiazole.

R_9 and R_{10} are independently each a cyano group, a tricyanopropene group, an ester group such as ethoxy carbonyl, methoxycarbonyl, etc., an acyl group such as benzoyl, carboxybenzoyl, etc., a carbamoyl group, or an alkylsulfonyl group such as ethylsulfonyl, methylsulfonyl, etc.

Examples of useful nuclei for Z_3 for Dye 1 structures include a 2-thio-2,4-oxazolidinedione nucleus (i.e., those of the 2-thio-2,4-(3H,5H)-oxazolidinedione series) (e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(3-carboxypropyl)-2-thio-2,4-oxazolidinedione, etc., a 2-thio-2,5-thiazolidinedione nucleus (i.e., the 2-thio-2,5-(3H,4H)-thiazolidinedione series) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.); a 2-thio-2,4-imidazolidinedione nucleus (i.e., 2-thiohydantoin) nucleus (e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.).

Examples of useful nuclei for Z₄, Z₅ and Z₆ for Dye 2 structures include a barbituric acid nucleus series (i.e., 1-carboxyethyl-3-methylbarbituric acid, 1-carboxyethyl-3-butylbarbituric acid, etc.); thianaphthenone nucleus (e.g., 2-(2H)-thianaphthenone, etc.); a 2,4-thiazolidinedione nucleus (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4-thiazolidinedione, 3-a-naphthyl-2,4-thiazolidinedione, etc.); a thiazolidinone nucleus (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3-a-naphthyl-4-thiazolidinone, etc.); a 2-thiazolin-4-one series (e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc.) a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) series (e.g., 2,4-imidazolidinedione (hydantoin) series (e.g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3-a-naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2,4-imidazolidinedione, 1-ethyl-2-a-naphthyl-2,4-imidazolidinedione, 1,3-diphenyl-2,4-imidazolidinedione, etc.).

R₁₁ represents a substituted or unsubstituted amino group (e.g., primary amino, anilino), or a substituted or unsubstituted aminoaryl group (e.g., dialkylaminophenyl).

According to the formulas, each M represents a substituted or unsubstituted methine group. Examples of substituents for the methine groups include alkyl (preferably of from 1 to 6 carbon atoms, e.g., methyl, ethyl, etc.) and aryl (e.g., phenyl). Additionally, substituents on the methine groups may form bridged linkages.

W₂ represents a counterion as necessary to balance the charge of the dye molecule. Such counterions include cations and anions for example sodium, potassium, triethylammonium, tetramethylguanidinium, diisopropylammonium, tetrabutylammonium, chloride, bromide, iodide, or paratoluene sulfonate. In a preferred embodiment the binary dye of formula I will have a net -1 charge and will have a counterion with a net +1 charge.

R₁ and R₂ are each independently substituted or unsubstituted aryl (preferably of 6 to 15 carbon atoms), or more preferably, substituted or unsubstituted alkyl (preferably of from 1 to 6 carbon atoms). Examples of aryl include phenyl, tolyl, p-chlorophenyl, and p-methoxyphenyl. Examples of alkyl include methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, decyl, dodecyl, etc., and substituted alkyl groups (preferably a substituted lower alkyl containing from 1 to 6 carbon atoms), such as a hydroxyalkyl group, e.g., 2-hydroxyethyl, 4-hydroxybutyl, etc., a carboxyalkyl group, e.g., 2-carboxyethyl, 4-carboxybutyl, etc., a sulfoalkyl group, e.g., 2-sulfoethyl, 3-sulfobutyl, 4-sulfobutyl, etc., a sulfatoalkyl group, etc., an acyloxyalkyl group, e.g., 2-acetoxyethyl, 3-acetoxypropyl, 4-butyroxybutyl, etc., an alkoxycarbonylalkyl group, e.g., 2-methoxycarbonylethyl, 4-ethoxycarbonylethyl, etc., or an aralkyl group, e.g., benzyl, phenethyl, etc. The alkyl or aryl group may be substituted by one or more of the substituents on the above-described substituted alkyl groups.

Dye 1 and Dye 2 useful in this invention for preparing the binary dyes can be prepared by methods known in the art. Such methods are taught, for example in M. Hamer, Cyanine Dyes and Related Compounds, Wiley, New York, 1964.

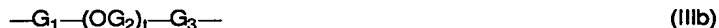
In accordance with this invention Dye 1 and Dye 2 are linked together by an organic hydrophilic linking group of the formula (IIIa):



wherein each of G₁, G₂, G₃ independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups (which can have one or more intervening heteroatoms) containing 1 to 20 carbon atoms, X is a heteroatom and t is 1-8. X is preferably -O- or -N(R₂₂)-, where R₂₂ is H, substituted or unsubstituted alkyl or substituted or unsubstituted aryl. The linking group can contain saturated or unsaturated rings, which can also contain heteroatoms. The unsaturated ring can be aromatic.

Particularly preferred linking groups are of the formula IIIa wherein at least one of G₁ or G₃ contains an amide, ester, sulfonamide, carbonate, urethane or carbamoyl group.

More Preferably, Dye 1 and Dye 2 are linked together by an organic linking group of one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing at least one ether oxygen atom. Preferred linking groups are of the formula (IIIb):



wherein each of G₁, G₂, G₃ independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing 1 to 20 carbon atoms and t is 1-8.

Particularly preferred linking groups are of the formula IIIb wherein: at least one of G₁ or G₃ contains an amide or ester group

More preferred linking groups are of the formula IIIb wherein: at least one of G₁ or G₃ contains an amide group.

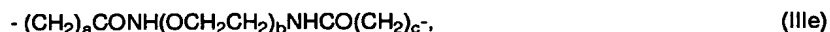
Other preferred linking groups are of the formula (IIIc):



EP 0 887 700 A1

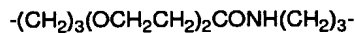
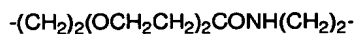
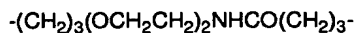
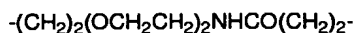
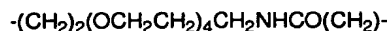
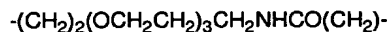
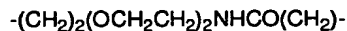
wherein each of G_1 , G_2 , G_3 independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing 1 to 20 carbon atoms and t is 1-8.

Particularly preferred linking groups are of the formula III'd or III'e:

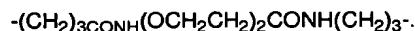


wherein: a , b and c are independently integers of 1 to 4.

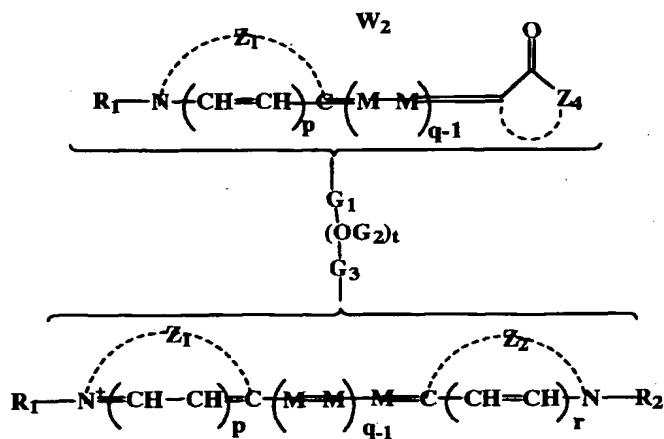
Examples of preferred linking groups are of the formula:



or



In a preferred embodiment of the invention dyes of formula I are of structures:



wherein:

Z_1 , Z_2 and Z_4 represent the atoms necessary to form a substituted or unsubstituted hetero ring and may be the same or different,
each M independently represents a substituted or unsubstituted methin group,
 q is a positive integer of from 1 to 4,

each p independently represents 0 or 1,

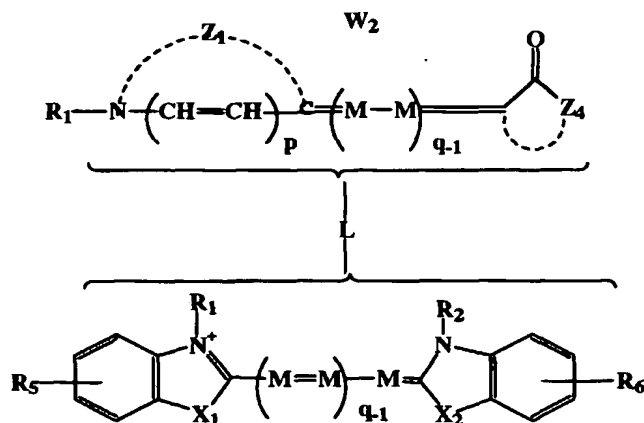
R₁ and R₂ each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl, and

W₂ is a counterion as necessary to balance the charge;

wherein each of G₁, G₂ and G₃ independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing 1 to 20 carbon atoms; and

t is a positive integer of from 1 to 6.

In a preferred embodiment of the invention dyes of formula I are of structures:



wherein:

Z₄ represent the atoms necessary to form a substituted or unsubstituted hetero ring,

each M independently represents a substituted or unsubstituted methine group,

q is a positive integer of from 1 to 4,

p represents a 0 or 1,

R₁ and R₂ each independently represents substituted or unsubstituted alkyl or unsubstituted aryl,

R₅ and R₆ each represent one or more substituents including possible fused aromatic rings, and

W₂ is a counterion as necessary to balance the charge;

L represents

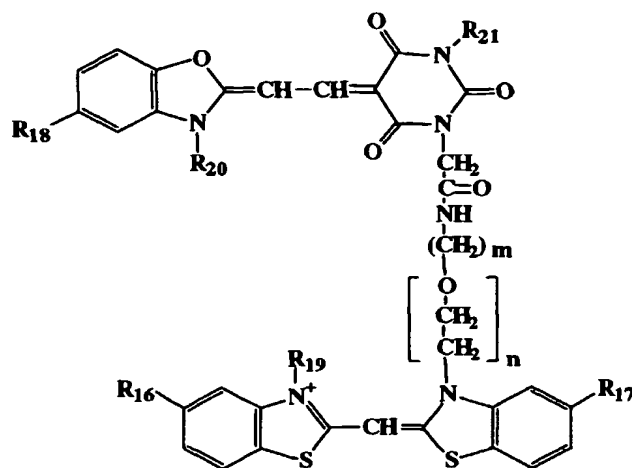


wherein:

each of G₁, G₂, G₃ independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing 1 to 20 carbon atoms and t is a positive integer of from 1 to 6. Each of G₁, G₂, G₃ can independently contain one or more saturated or unsaturated rings.

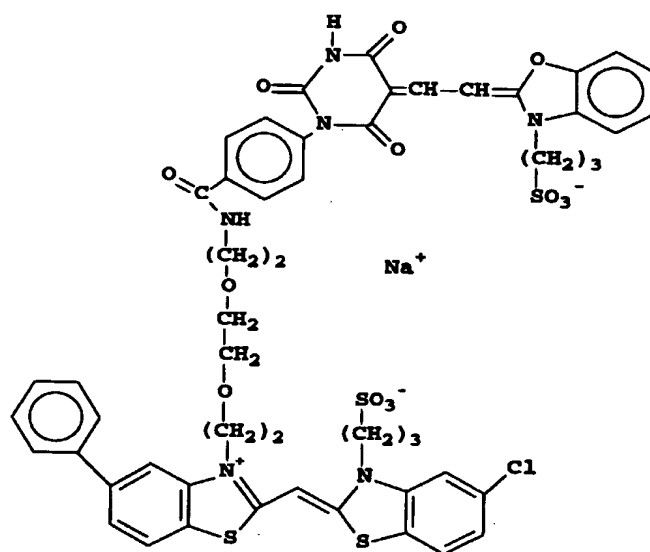
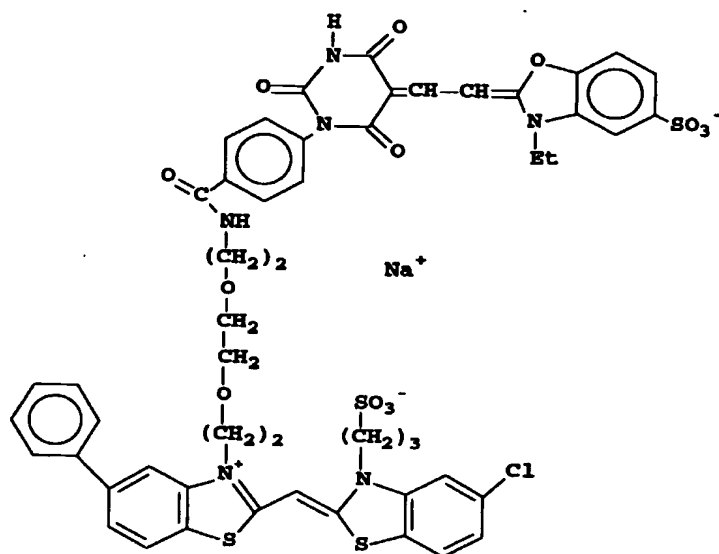
Examples of particularly preferred dyes of formula I are listed in the Table I below.

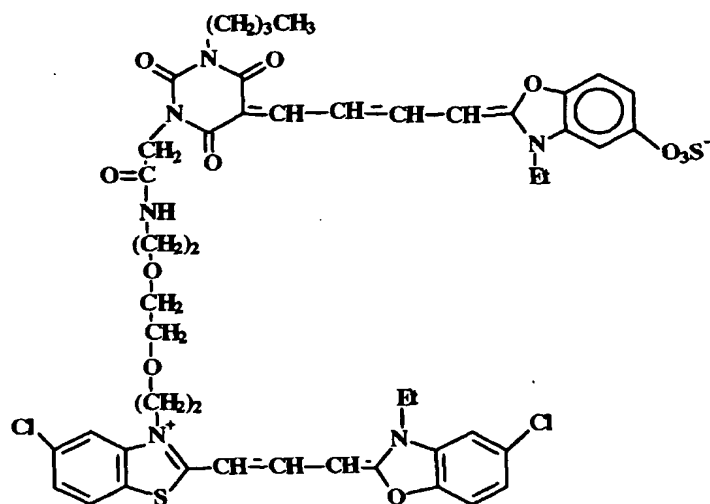
Table I. Invention Dyes



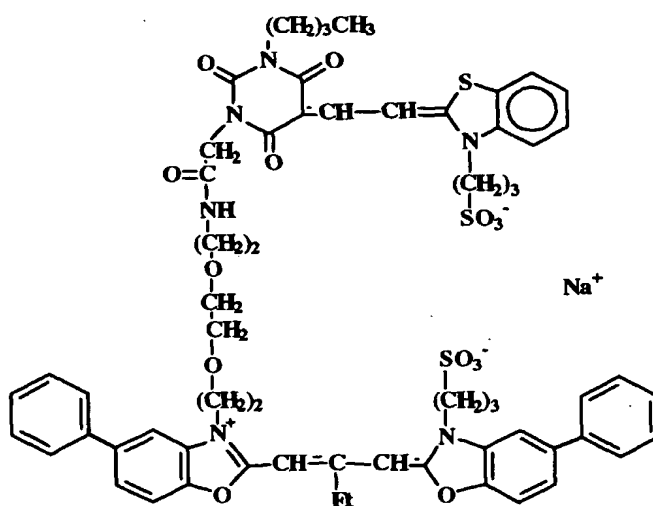
Dye	R ₁₆	R ₁₇	R ₁₈	R ₁₉	R ₂₀	R ₂₁	m	n
I-1	Cl	Ph	SO ₃ ⁻	(CH ₂) ₃ SO ₃ ⁻	Et	Bu	2	2
I-2	Cl	Cl	SO ₃ ⁻	(CH ₂) ₃ SO ₃ ⁻	Et	Bu	2	2
I-3	Cl	Py	SO ₃ ⁻	(CH ₂) ₃ SO ₃ ⁻	Et	Bu	2	2
I-4	Cl	Ph	SO ₃ ⁻	(CH ₂) ₃ SO ₃ ⁻	Et	Bu	3	3
I-5	Cl	Ph	SO ₃ ⁻	(CH ₂) ₃ SO ₃ ⁻	Et	Bu	3	4

Ph is phenyl, Py is pyrrole-1-yl, Cl is chloro, Et is ethyl, Bu is butyl

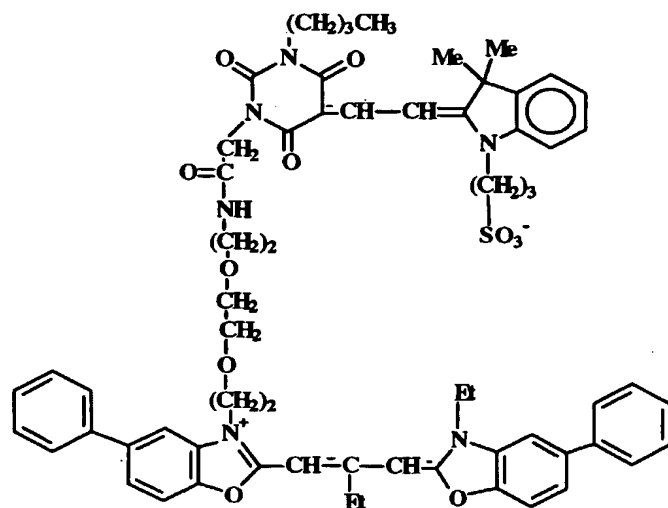




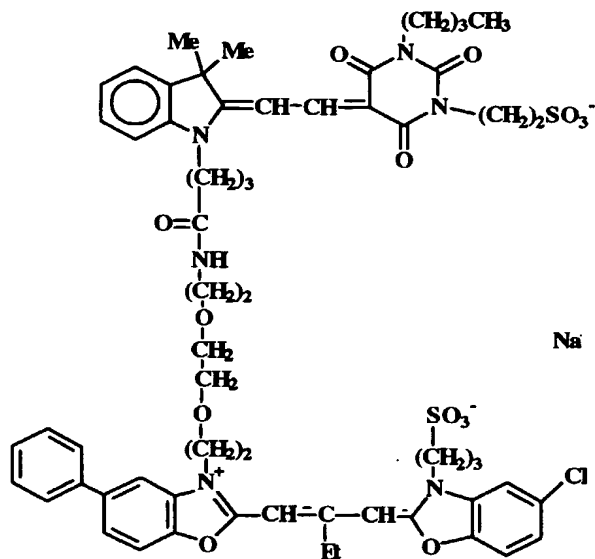
I-8



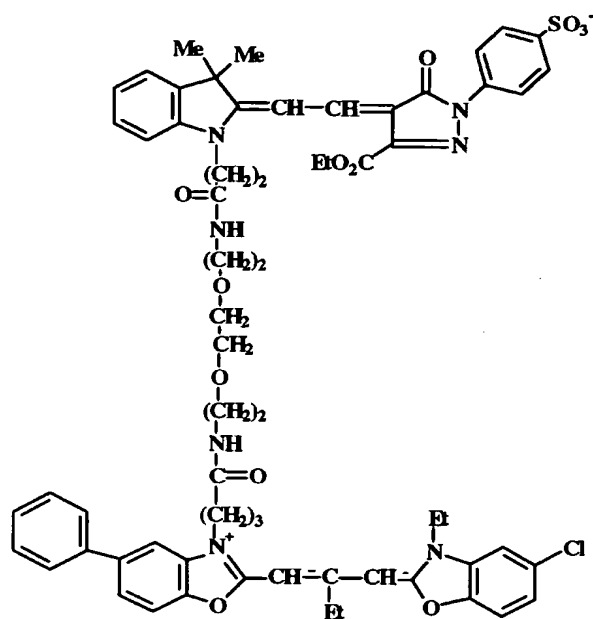
I-9



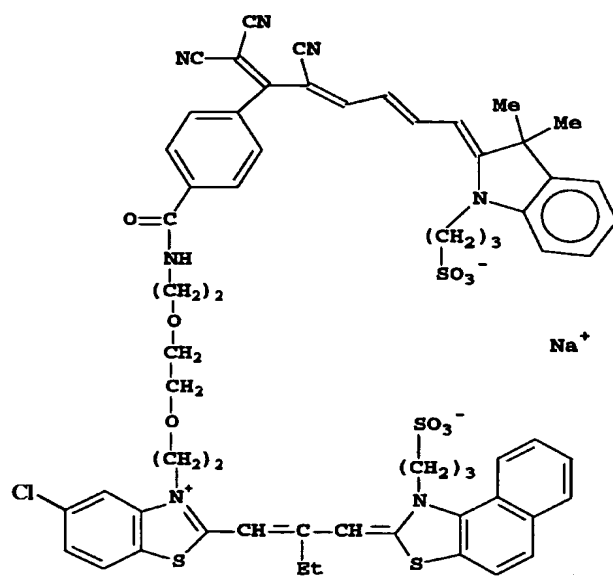
I-10



I-11

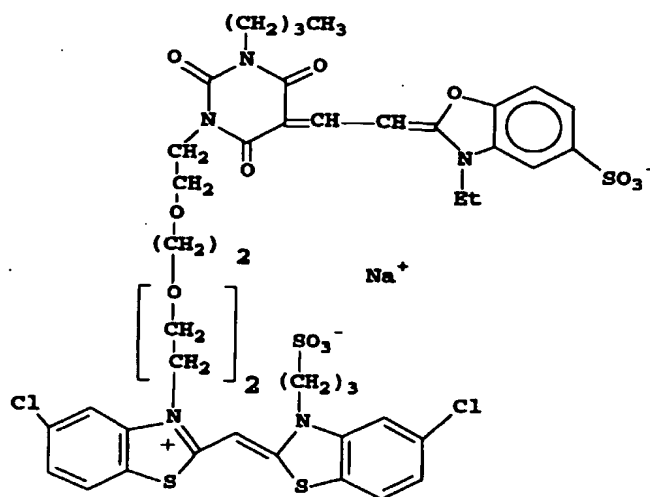


I-12

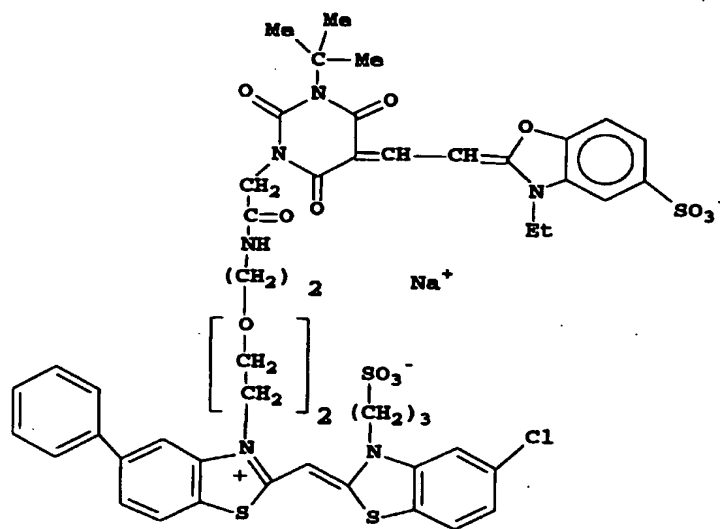


I-13

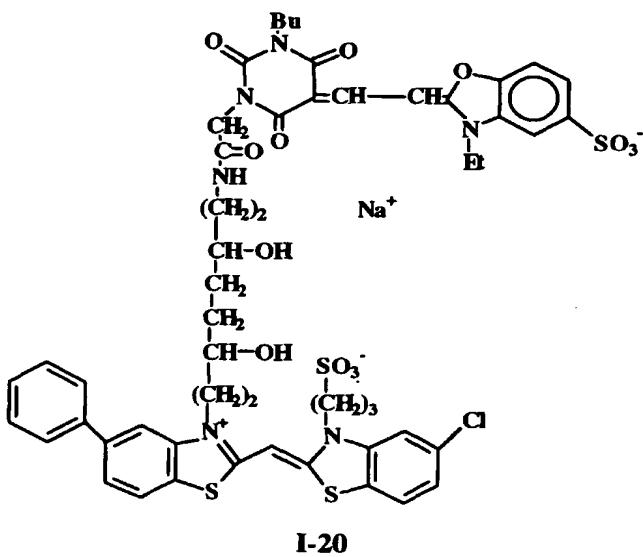
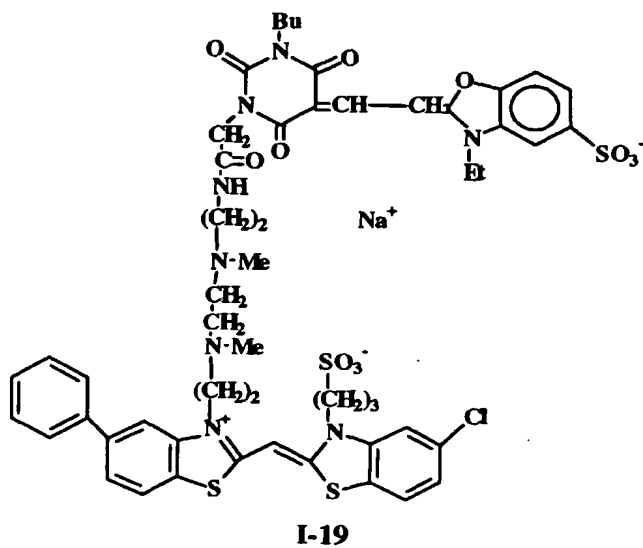


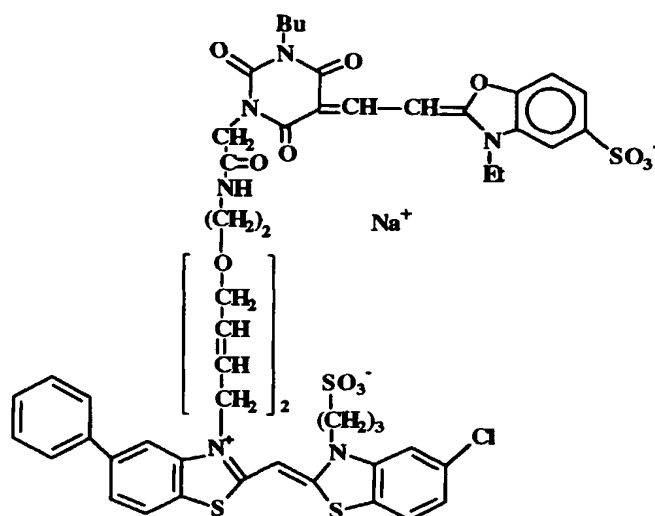


I-16

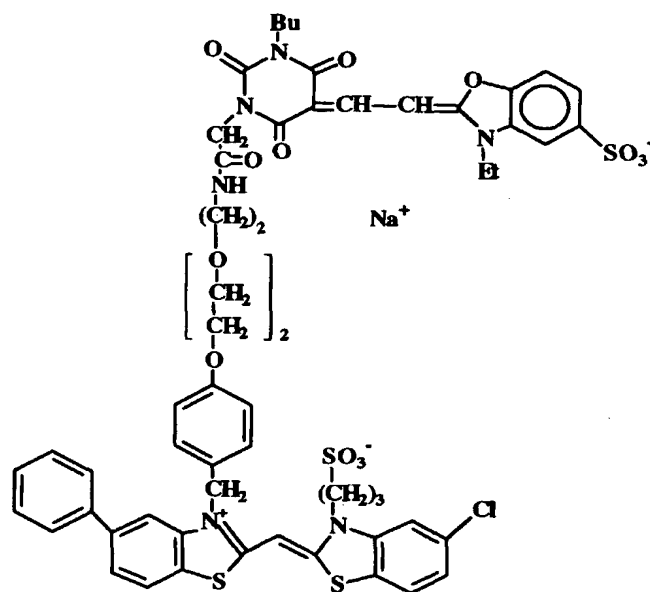


I-18

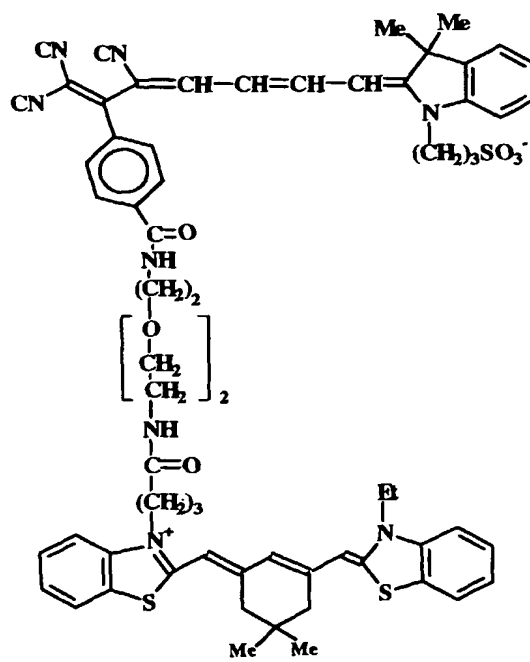
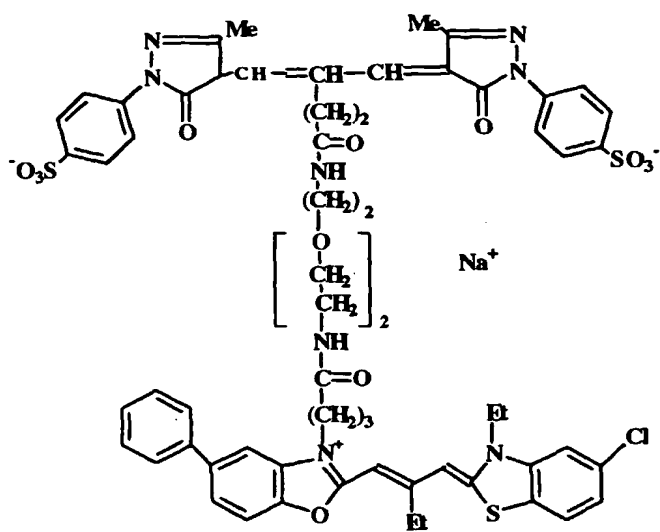


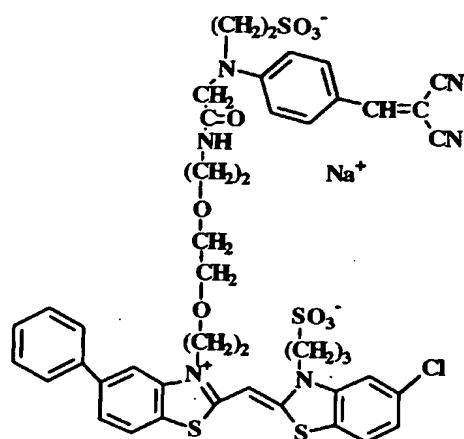


I-21

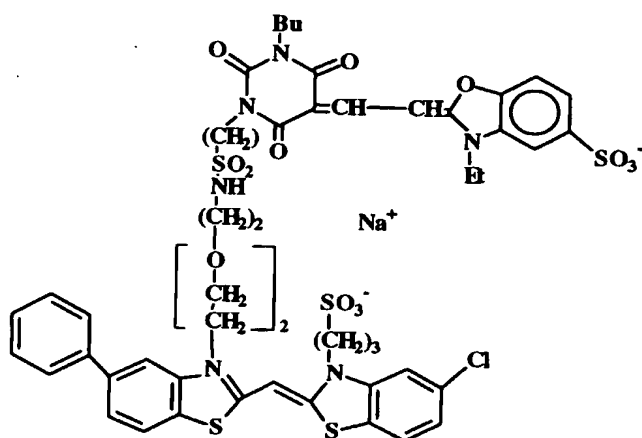


I-22



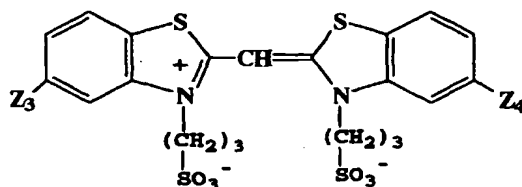


I-25



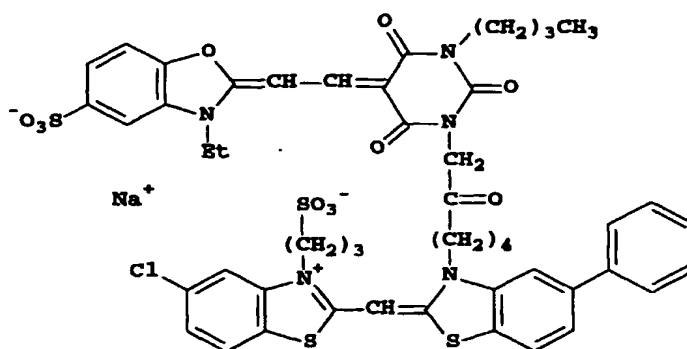
I-26

Table II. Comparison Dyes



Dye	Z ₃	Z ₄
C-1	Cl	Ph
C-2	Cl	Cl
C-3	Cl	Py

Ph is phenyl, Py is pyrrole-1-yl, Cl is chloro,



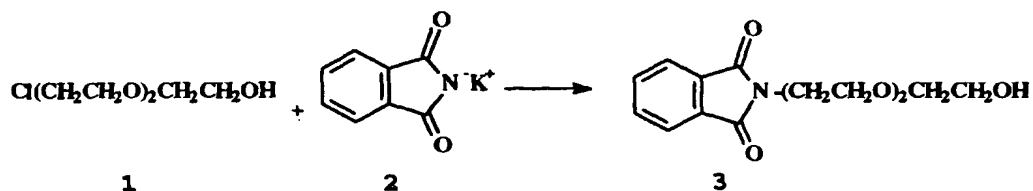
C-4

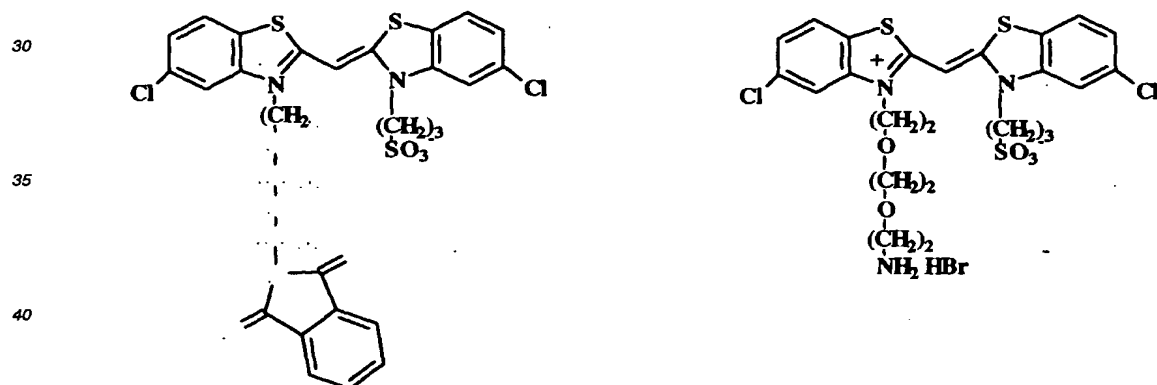
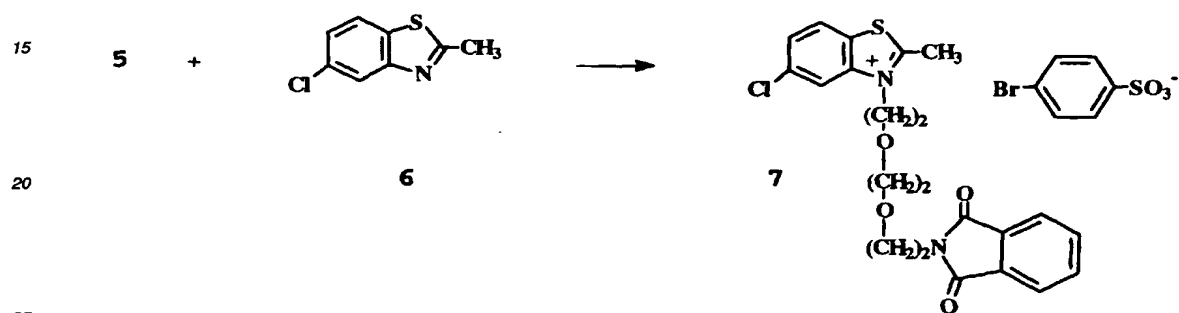
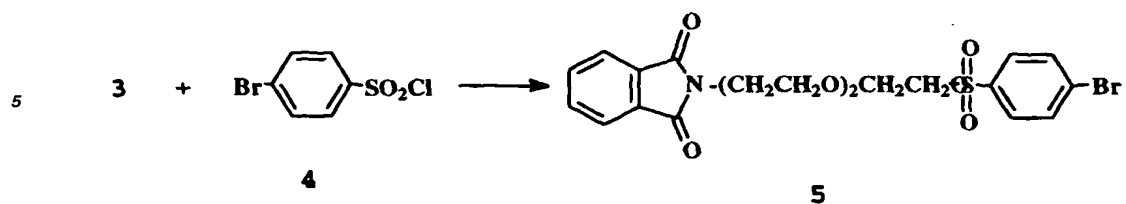
Dye 1 and Dye 2 can be prepared according to techniques that are well-known in the art, such as described in Hamer, Cyanine Dyes and Related Compounds, 1964 (publisher John Wiley & Sons, New York, NY) and T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977. The binary dyes of this invention can be prepared by linking Dye 1 with Dye 2. This can be accomplished by various methods. For example, if one dye contains a hydrophilic chain with an amino functional group and the other dye contains a carboxylic acid group then the dyes can be linked by forming an amide group. The formation of amide groups has been examined extensively by peptide chemists and many methods have been developed for this type of reaction (see J. March, Advanced Organic Chemistry, John Wiley and Sons, Inc., New York, 1985 and references cited therein.)

The following examples further illustrates the invention:

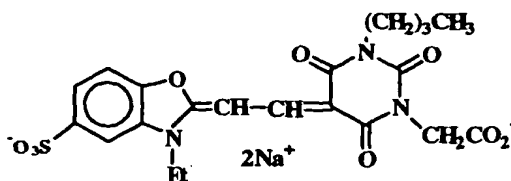
Example 1 (Preparation of Dye I-2)

A dye substituted with a hydrophilic linking group containing a terminal amino functional group (for example Dye A) can be prepared as shown below. Reaction of 2-[2-(2-chloroethoxy)ethoxy]ethanol, 1, with potassium phthalimide, 2, affords alcohol 3 (H. Maeda, S. Furuyoshi, Y. Nakatsuji, and M. Okahara, Tetrahedron, 38, 3359 (1982)). The brosylate 5, can be prepared by standard methods by reacting 3 with p-bromobenzenesulfonyl chloride 4, (for example see L. F. Fieser and M. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, Inc., New York, 1967.) Compound 5 is an alkylating agent and reaction with a base such as 6 affords a quaternary salt, 7. This type of quaternary salt can be used to make a variety of dyes, such as described in Hamer, Cyanine Dyes and Related Compounds, 1964 (publisher John Wiley & Sons, New York, NY). For example, Dye 8 can be prepared readily. Removal of the phthalimide protecting group affords Dye A (for the use and removal of phthalimide protecting groups see J. March, Advanced Organic Chemistry, John Wiley and Sons, Inc., New York, 1985 and references cited therein.)





45 Dyes such as Dye B can be prepared according to techniques that are well-known in the art, such as described in Hamer, Cyanine Dyes and Related Compounds, 1964 (publisher John Wiley & Sons, New York, NY) and T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977.



Dye B

Binary Dye Preparation - Linking Dye A and Dye B:

Dye A (4.5 g, 6.6 mmol), Dye B (3.8 g, 7.1 mmol) and 1-hydroxy-benzotriazole (0.93 g, 6.9 mmol) were combined with 150 mL of dimethylsulfoxide in a 250 mL 3-necked round-bottomed flask equipped with a thermometer, nitrogen inlet, and magnetic stirring. The reaction mixture was placed in an oil bath at 60°C. When internal temperature reached 55°C a yellow solution had formed. O-Benzotriazol-1-yl-N,N,N',N'-tetramethyluronium tetrafluoroborate (2.6 g, 6.9 mmol) was added and the mixture was stirred for 5 min. Diisopropylethylamine was then added (3.6 mL, 20.9 mmol) and the mixture was stirred for 2.5 h at 60° - 65°C. The heat was removed and the mixture was stirred overnight. The reaction mixture was transferred to a 500 mL erlenmeyer and diluted to 850 mL with acetone. The yellow precipitate formed was collected and recrystallized from methanol containing sodium acetate. This afforded 3.9 g (54% yield) of product dye I-2, Table I, λ_{max} (MeOH) = 433 nm, $\epsilon = 14.7 \times 10^4$.

Anal. Calcd for $\text{C}_{45}\text{H}_{47}\text{Cl}_2\text{N}_6\text{O}_{13}\text{S}_4\text{-Na-5H}_2\text{O}$:	C, 45.30;	H, 4.78;	N, 7.05
Found:	C, 45.09;	H, 4.42;	N, 6.86

In combination with the dyes of the invention, the silver halide may be sensitized by additional sensitizing dyes such as described in Research Disclosure, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND; The Theory of the Photographic Process, T.H. James, editor, 4th Edition, Macmillan, New York, 1977, Chapter 8; and in F. M. Hamer, Cyanine Dyes and Related Compounds, Wiley, New York, 1964.

The sensitizing dyes may be present in the emulsion together with dyes which themselves do not give rise to spectrally sensitizing effects but exhibit a supersensitizing effect or materials which do not substantially absorb visible light but exhibit a supersensitizing effect. For example, aminostilbene compounds substituted with a nitrogen-containing heterocyclic group (e.g., those described in U.S. Patent Nos. 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (e.g., those described in U.S. Patent No. 3,743,510), cadmium salts, or azaindene compounds, can be present.

The dye may be added to an emulsion of the silver halide grains and a hydrophilic colloid at any time prior to (e.g., during or after chemical sensitization) or simultaneous with the coating of the emulsion on a photographic element). The dye/silver halide emulsion may be mixed with a dispersion of color image-forming coupler immediately before coating or in advance of coating (for example, 2 hours). The above-described sensitizing dyes can be used individually, or may be used in combination, e.g. to also provide the silver halide with additional sensitivity to wavelengths of light outside that provided by one dye or to supersensitize the silver halide.

The emulsion layer of the photographic element of the invention can comprise any one or more of the light sensitive layers of the photographic element. The photographic elements made in accordance with the present invention can be black and white elements, single color elements or multicolor elements. Multicolor elements contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least on red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming cou-

pler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers. All of these can be coated on a support which can be transparent or reflective (for example, a paper support).

Photographic elements of the present invention may also usefully include a magnetic recording material as described in Research Disclosure, Item 34390, November 1992, or a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support as in US 4,279,945 and US 4,302,523. The element typically will have a total thickness (excluding the support) of from 5 to 30 microns. While the order of the color sensitive layers can be varied, they will normally be red-sensitive, green-sensitive and blue-sensitive, in that order on a transparent support, (that is, blue sensitive furthest from the support) and the reverse order on a reflective support being typical.

The present invention also contemplates the use of photographic elements of the present invention in what are often referred to as single use cameras (or "film with lens" units). These cameras are sold with film preloaded in them and the entire camera is returned to a processor with the exposed film remaining inside the camera. Such cameras may have glass or plastic lenses through which the photographic element is exposed.

In the following discussion of suitable materials for use in elements of this invention, reference will be made to Research Disclosure, September 1996, Number 389, Item 38957, which will be identified hereafter by the term "Research Disclosure I." The Sections hereafter referred to are Sections of the Research Disclosure I unless otherwise indicated. All Research Disclosures referenced are published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire PO10 7DQ, ENGLAND.

The silver halide emulsions employed in the photographic elements of the present invention may be negative-working, such as surface-sensitive emulsions or unfogged internal latent image forming emulsions, or positive working emulsions of the internal latent image forming type (that are fogged during processing). Suitable emulsions and their preparation as well as methods of chemical and spectral sensitization are described in Sections I through V. Color materials and development modifiers are described in Sections V through XX. Vehicles which can be used in the photographic elements are described in Section II, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described, for example, in Sections VI through XIII. Manufacturing methods are described in all of the sections, layer arrangements particularly in Section XI, exposure alternatives in Section XVI, and processing methods and agents in Sections XIX and XX.

With negative working silver halide a negative image can be formed. Optionally a positive (or reversal) image can be formed although a negative image is typically first formed.

The photographic elements of the present invention may also use colored couplers (e.g. to adjust levels of inter-layer correction) and masking couplers such as those described in EP 213 490; Japanese Published Application 58-172,647; U.S. Patent 2,983,608; German Application DE 2,706,117C; U.K. Patent 1,530,272; Japanese Application A-113935; U.S. Patent 4,070,191 and German Application DE 2,643,965. The masking couplers may be shifted or blocked.

The photographic elements may also contain materials that accelerate or otherwise modify the processing steps of bleaching or fixing to improve the quality of the image. Bleach accelerators described in EP 193 389; EP 301 477; U.S. 4,163,669; U.S. 4,865,956; and U.S. 4,923,784 are particularly useful. Also contemplated is the use of nucleating agents, development accelerators or their precursors (UK Patent 2,097,140; U.K. Patent 2,131,188); development inhibitors and their precursors (U.S. Patent No. 5,460,932; U.S. Patent No. 5,478,711); electron transfer agents (U.S. 4,859,578; U.S. 4,912,025); antifogging and anti color-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols; and non color-forming couplers.

The elements may also contain filter dye layers comprising colloidal silver sol or yellow and/or magenta filter dyes and/or antihalation dyes (particularly in an undercoat beneath all light sensitive layers or in the side of the support opposite that on which all light sensitive layers are located) either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. 4,366,237; EP 096 570; U.S. 4,420,556; and U.S. 4,543,323.) Also, the couplers may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. 5,019,492.

The photographic elements may further contain other image-modifying compounds such as "Development Inhibitor-Releasing" compounds (DIR's). Useful additional DIR's for elements of the present invention, are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publica-

tions GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063; DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346,899; 362,870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

DIR compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in *Photographic Science and Engineering*, Vol. 13, p. 174 (1969).

It is also contemplated that the concepts of the present invention may be employed to obtain reflection color prints as described in *Research Disclosure*, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire PO101 7DQ, England. The emulsions and materials to form elements of the present invention, may be coated on pH adjusted support as described in U.S. 4,917,994; with epoxy solvents (EP 0 164 961); with additional stabilizers (as described, for example, in U.S. 4,346,165; U.S. 4,540,653 and U.S. 4,906,559); with ballasted chelating agents such as those in U.S. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium; and with stain reducing compounds such as described in U.S. 5,068,171 and U.S. 5,096,805. Other compounds which may be useful in the elements of the invention are disclosed in Japanese Published Applications 83-09,959; 83-62,586; 90-072,629; 90-072,630; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,096; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-101,937; 90-103,409; 90-151,577.

The silver halide used in the photographic elements may be, for example, silver iodobromide, silver bromide, silver chloride, silver chlorobromide, or silver chloriodobromide.

The type of silver halide grains preferably include polymorphic, cubic, and octahedral. The grain size of the silver halide may have any distribution known to be useful in photographic compositions, and may be either polydispersed or monodispersed.

Tabular grain silver halide emulsions may also be used. Tabular grains are those with two parallel major faces each clearly larger than any remaining grain face and tabular grain emulsions are those in which the tabular grains account for at least 30 percent, more typically at least 50 percent, preferably >70 percent and optimally >90 percent of total grain projected area. The tabular grains can account for substantially all (>97 percent) of total grain projected area. The tabular grain emulsions can be high aspect ratio tabular grain emulsions--i.e., $ECD/t > 8$, where ECD is the diameter of a circle having an area equal to grain projected area and t is tabular grain thickness; intermediate aspect ratio tabular grain emulsions--i.e., $ECD/t = 5$ to 8; or low aspect ratio tabular grain emulsions--i.e., $ECD/t = 2$ to 5. The emulsions typically exhibit high tabularity (T), where T (i.e., ECD/t^2) > 25 and ECD and t are both measured in micrometers (μm). The tabular grains can be of any thickness compatible with achieving an aim average aspect ratio and/or average tabularity of the tabular grain emulsion. Preferably the tabular grains satisfying projected area requirements are those having thicknesses of <0.3 μm , thin (<0.2 μm) tabular grains being specifically preferred and ultrathin (<0.07 μm) tabular grains being contemplated for maximum tabular grain performance enhancements. When the native blue absorption of iodohalide tabular grains is relied upon for blue speed, thicker tabular grains, typically up to 0.5 μm in thickness, are contemplated.

High iodide tabular grain emulsions are illustrated by House U.S. Patent 4,490,458, Maskasky U.S. Patent 4,459,353 and Yagi et al EPO 0 410 410.

Tabular grains formed of silver halide(s) that form a face centered cubic (rock salt type) crystal lattice structure can have either {100} or {111} major faces. Emulsions containing {111} major face tabular grains, including those with controlled grain dispersities, halide distributions, twin plane spacing, edge structures and grain dislocations as well as adsorbed {111} grain face stabilizers, are illustrated in those references cited in *Research Disclosure I*, Section I.B.(3) (page 503).

The silver halide grains to be used in the invention may be prepared according to methods known in the art, such as those described in *Research Disclosure I* and James, *The Theory of the Photographic Process*. These include methods such as ammoniacal emulsion making, neutral or acidic emulsion making, and others known in the art. These methods generally involve mixing a water soluble silver salt with a water soluble halide salt in the presence of a protective colloid, and controlling the temperature, pAg, pH values, etc, at suitable values during formation of the silver halide by precipitation.

In the course of grain precipitation one or more dopants (grain occlusions other than silver and halide) can be introduced to modify grain properties. For example, any of the various conventional dopants disclosed in *Research Disclosure*, Item 38957, Section I. Emulsion grains and their preparation, sub-section G. Grain modifying conditions and adjustments, paragraphs (3), (4) and (5), can be present in the emulsions of the invention. In addition it is specifically contemplated to dope the grains with transition metal hexacoordination complexes containing one or more organic ligands, as taught by Olm et al U.S. Patent 5,360,712.

It is specifically contemplated to incorporate in the face centered cubic crystal lattice of the grains a dopant capable of increasing imaging speed by forming a shallow electron trap (hereinafter also referred to as a SET) as discussed in

Research Disclosure Item 36736 published November 1994, here incorporated by reference.

The SET dopants are effective at any location within the grains. Generally better results are obtained when the SET dopant is incorporated in the exterior 50 percent of the grain, based on silver. An optimum grain region for SET incorporation is that formed by silver ranging from 50 to 85 percent of total silver forming the grains. The SET can be introduced all at once or run into the reaction vessel over a period of time while grain precipitation is continuing. Generally SET forming dopants are contemplated to be incorporated in concentrations of at least 1×10^{-7} mole per silver mole up to their solubility limit, typically up to about 5×10^{-4} mole per silver mole.

SET dopants are known to be effective to reduce reciprocity failure. In particular the use of iridium hexacoordination complexes or Ir^{+4} complexes as SET dopants is advantageous.

Iridium dopants that are ineffective to provide shallow electron traps (non-SET dopants) can also be incorporated into the grains of the silver halide grain emulsions to reduce reciprocity failure. To be effective for reciprocity improvement the Ir can be present at any location within the grain structure. A preferred location within the grain structure for Ir dopants to produce reciprocity improvement is in the region of the grains formed after the first 60 percent and before the final 1 percent (most preferably before the final 3 percent) of total silver forming the grains has been precipitated. The dopant can be introduced all at once or run into the reaction vessel over a period of time while grain precipitation is continuing. Generally reciprocity improving non-SET Ir dopants are contemplated to be incorporated at their lowest effective concentrations.

The contrast of the photographic element can be further increased by doping the grains with a hexacoordination complex containing a nitrosyl or thionitrosyl ligand (NZ dopants) as disclosed in McDugle et al U.S. Patent 4,933,272.

The contrast increasing dopants can be incorporated in the grain structure at any convenient location. However, if the NZ dopant is present at the surface of the grain, it can reduce the sensitivity of the grains. It is therefore preferred that the NZ dopants be located in the grain so that they are separated from the grain surface by at least 1 percent (most preferably at least 3 percent) of the total silver precipitated in forming the silver iodochloride grains. Preferred contrast enhancing concentrations of the NZ dopants range from 1×10^{-11} to 4×10^{-8} mole per silver mole, with specifically preferred concentrations being in the range from 10^{-10} to 10^{-8} mole per silver mole.

Although generally preferred concentration ranges for the various SET, non-SET Ir and NZ dopants have been set out above, it is recognized that specific optimum concentration ranges within these general ranges can be identified for specific applications by routine testing. It is specifically contemplated to employ the SET, non-SET Ir and NZ dopants singly or in combination. For example, grains containing a combination of an SET dopant and a non-SET Ir dopant are specifically contemplated. Similarly SET and NZ dopants can be employed in combination. Also NZ and in dopants that are not SET dopants can be employed in combination. Finally, the combination of a non-SET Ir dopant with a SET dopant and an NZ dopant. For this latter three-way combination of dopants it is generally most convenient in terms of precipitation to incorporate the NZ dopant first, followed by the SET dopant, with the non-SET Ir dopant incorporated last.

The photographic elements of the present invention, as is typical, provide the silver halide in the form of an emulsion. Photographic emulsions generally include a vehicle for coating the emulsion as a layer of a photographic element. Useful vehicles include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g., cellulose esters), gelatin (e.g., alkali-treated gelatin such as cattle bone or hide gelatin, or acid treated gelatin such as pigskin gelatin), deionized gelatin, gelatin derivatives (e.g., acetylated gelatin, phthalated gelatin), and others as described in Research Disclosure I. Also useful as vehicles or vehicle extenders are hydrophilic water-permeable colloids. These include synthetic polymeric peptizers, carriers, and/or binders such as poly(vinyl alcohol), poly(vinyl lactams), acrylamide polymers, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, and methacrylamide copolymers, as described in Research Disclosure I. The vehicle can be present in the emulsion in any amount useful in photographic emulsions. The emulsion can also include any of the addenda known to be useful in photographic emulsions.

The silver halide to be used in the invention may be advantageously subjected to chemical sensitization. Compounds and techniques useful for chemical sensitization of silver halide are known in the art and described in Research Disclosure I and the references cited therein. Compounds useful as chemical sensitizers, include, for example, active gelatin, sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhenium, phosphorous, or combinations thereof. Chemical sensitization is generally carried out at pAg levels of from 5 to 10, pH levels of from 4 to 8, and temperatures of from 30 to 80°C, as described in Research Disclosure I, Section IV (pages 510-511) and the references cited therein.

The silver halide may be sensitized by sensitizing dyes by any method known in the art, such as described in Research Disclosure I. The dye may be added to an emulsion of the silver halide grains and a hydrophilic colloid at any time prior to (e.g., during or after chemical sensitization) or simultaneously with the coating of the emulsion on a photographic element. The dyes may, for example, be added as a solution in water or an alcohol. The dye/silver halide emulsion may be mixed with a dispersion of color image-forming coupler immediately before coating or in advance of coating (for example, 2 hours).

Photographic elements of the present invention are preferably imagewise exposed using any of the known techniques, including those described in Research Disclosure I, section XVI. This typically involves exposure to light in the visible region of the spectrum, and typically such exposure is of a live image through a lens, although exposure can also be exposure to a stored image (such as a computer stored image) by means of light emitting devices (such as light emitting diodes and CRTs).

Photographic elements comprising the composition of the invention can be processed in any of a number of well-known photographic processes utilizing any of a number of well-known processing compositions, described, for example, in Research Disclosure I, or in T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977. In the case of processing a negative working element, the element is treated with a color developer (that is one which will form the colored image dyes with the color couplers), and then with an oxidizer and a solvent to remove silver and silver halide. In the case of processing a reversal color element, the element is first treated with a black and white developer (that is, a developer which does not form colored dyes with the coupler compounds) followed by a treatment to fog silver halide (usually chemical fogging or light fogging), followed by treatment with a color developer. Preferred color developing agents are p-phenylenediamines. Especially preferred are:

4-amino N,N-diethylaniline hydrochloride,
 4-amino-3-methyl-N,N-diethylaniline hydrochloride,
 4-amino-3-methyl-N-ethyl-N-(b-(methanesulfonamido)ethylaniline sesquisulfate hydrate,
 4-amino-3-methyl-N-ethyl-N-(b-hydroxyethyl)aniline sulfate,
 4-amino-3-b-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride and
 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid.

Dye images can be formed or amplified by processes which employ in combination with a dye-image-generating reducing agent an inert transition metal-ion complex oxidizing agent, as illustrated by Bissonette U.S. Patents 3,748,138, 3,826,652, 3,862,842 and 3,989,526 and Travis U.S. Patent 3,765,891, and/or a peroxide oxidizing agent as illustrated by Matejec U.S. Patent 3,674,490, *Research Disclosure*, Vol. 116, December, 1973, Item 11660, and Bissonette *Research Disclosure*, Vol. 148, August, 1976, Items 14836, 14846 and 14847. The photographic elements can be particularly adapted to form dye images by such processes as illustrated by Dunn et al U.S. Patent 3,822,129, Bissonette U.S. Patents 3,834,907 and 3,902,905, Bissonette et al U.S. Patent 3,847,619, Mowrey U.S. Patent 3,904,413, Hirai et al U.S. Patent 4,880,725, Iwano U.S. Patent 4,954,425, Marsden et al U.S. Patent 4,983,504, Evans et al U.S. Patent 5,246,822, Twist U.S. Patent No. 5,324,624, Fyson EPO 0 487 616, Tannahill et al WO 90/13059, Marsden et al WO 90/13061, Grimsey et al WO 91/16666, Fyson WO 91/17479, Marsden et al WO 92/01972, Tannahill WO 92/05471, Henson WO 92/07299, Twist WO 93/01524 and WO 93/11460 and Wingender et al German OLS 4,211,460.

Development is followed by bleach-fixing, to remove silver or silver halide, washing and drying.

Photographic Evaluation

Example 1

Film coating evaluations were carried out in a color format on a sulfur-and-gold sensitized 0.54 μ m silver bromoiodide emulsion (see Table III for results). Dyes were added at 0.6 mmole dye/Ag mole before the chemical finish. The emulsion was combined with a coupler dispersion containing 2-(2,4-bis(1,1-dimethylpropyl)phenoxy)-N-(4-(((4-cyanophenyl)amino)carbonyl)amino)-3-hydroxyphenyl)-hexanamide just prior to coating. Single-layer coatings were made on remjet-backed acetate support. Sensitometric exposures (0.1 sec) were done using 365 nm Hg-line exposure or a tungsten exposure with filtration to simulate a daylight exposure. The described elements were processed in the known C-41 color process as described in *Brit. J. Photog. Annual* of 1988, p191-198 with the exception that the composition of the bleach solution was changed to comprise propylenediaminetetraacetic acid.

Unprocessed coatings were examined spectroscopically to determine light absorption properties. To determine the spectral photographic sensitivity distribution, the coatings were given a 0.1 sec exposure on a wedge spectrographic instrument covering a wavelength range from 350 to 750 nm. The instrument contains a tungsten light source and a step tablet ranging in density from 0 to 3 density units in 0.3 density steps. Correction for the instrument's variation in spectral irradiance with wavelength was done via computer. After processing, a plot of log relative spectral sensitivity vs. wavelength can be obtained. The results are reported in Table III.

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Table III

Sensitometric Speed* Evaluation of Dyes on a AgBr(I) Cubic Emulsion							
Sample	Dye	Speed				Sensitization Envelope	Remarks
		365L ^a	DL ^b	(DL-365L) ^c	Δ Speed ^d		
1	C-1	173	190	17	-	Narrow	Comparison
2	I-1	180	202	22	5	Broad	Invention

*speed is reported in 100 x logE units.

^aspeed from a 365 line exposure.

^bspeed from an exposure that simulates daylight.

^cthe daylight speed of the sample minus the 365 line speed of the sample - this corrects for minor differences in the chemical sensitization and gives a better measure of dye performance.

^d Δ Speed is the speed of the sample minus the speed of the example comparison.

Example 2

Film coating evaluations were carried out in a color format as described in Example 1, except the emulsion was a sulfur-and-gold sensitized 2.6 x 0.06 μm AgBrI tabular emulsion and the exposure time was 0.02 sec. Dyes were added at 1.7 mmole dye/Ag mole before the chemical finish (see Table IV for results).

Table IV

Sensitometric Speed* Evaluation of Dyes on a AgBr(I) Tabular Emulsion							
Sample	Dye	Speed				Sensitization Envelope	Remarks
		365L ^a	DL ^b	(DL-365L) ^c	Δ Speed ^d		
1	C-1	236	229	-7	-	Narrow	Comparison
2	I-1	245	247	2	9	Broad	Invention
3	C-2	254	242	-12	-	Narrow	Comparison
4	I-2	253	252	-1	11	Broad	Invention

*speed is reported in 100 x logE units.

^aspeed from a 365 line exposure.

^bspeed from an exposure that simulates daylight.

^cthe daylight speed of the sample minus the 365 line speed of the sample - this corrects for minor differences in the chemical sensitization and gives a better measure of dye performance.

^d Δ Speed is the speed of the sample minus the speed of the example comparison.

Example 3

Film coating evaluations were carried out in a color format as described in Example 2, see Table V for results.

Table V

Sensitometric Speed* Evaluation of Dyes on a AgBr(I) Tabular							
				Speed		Sensitization Envelope	
Sample	Dye	365L ^a	DL ^b	(DL-365L) ^c	Δ Speed ^d		Remarks
1	C-1	229	224	-5	-	Narrow	Comparison
2	I-1	241	241	0	5	Broad	Invention
3	I-6	258	259	1	6	Broad	Invention
4	I-7	237	237	0	5	Broad	Invention
5	C-3	230	232	2	-	Narrow	Comparison
6	I-3	228	233	5	3	Broad	Invention

*speed is reported in $100 \times \log E$ units.

^aspeed from a 365 line exposure.

^bspeed from an exposure that simulates daylight.

^cthe daylight speed of the sample minus the 365 line speed of the sample - this corrects for minor differences in the chemical sensitization and gives a better measure of dye performance.

^d Δ Speed is the speed of the sample minus the speed of the example comparison.

Example 4

Film coating evaluations were carried out in a color format as described in Example 2, see Table VI for results.

Table VI

Sensitometric Speed* Evaluation of Dyes on a AgBr(I) Tabular Emulsion							
				Speed		Sensitization Envelope	
Sample	Dye	365L ^a	DL ^b	(DL-365L) ^c	Δ Speed ^d		Remarks
2	C-4	225	191	-34	-	Broad	Comparison
3	I-1	239	238	-1	33	Broad	Invention

*speed is reported in $100 \times \log E$ units.

^aspeed from a 365 line exposure.

^bspeed from an exposure that simulates daylight.

^cthe daylight speed of the sample minus the 365 line speed of the sample - this corrects for minor differences in the chemical sensitization and gives a better measure of dye performance.

^d Δ Speed is the speed of the sample minus the speed of the example comparison.

It can be seen from Examples 1-3 that the dyes of the invention give higher speed than the comparison dyes. The dyes of the invention also give a broader sensitization envelope. For example Fig. 1 a shows the light absorption profile and Fig 1b shows the spectral sensitivity of Dye I-1 compared to Dye C-1. This broad sensitivity is highly desirable for color reproduction because it makes the photographic element less susceptible variations in the light source. For example, photographic elements containing the dyes of the invention will be able to reproduce scenes illuminated with either daylight or fluorescent light whereas photographic elements containing the comparison dyes will have relatively poor sensitivity to scenes illuminated with fluorescent light.

It can be seen from Example 4 that when compared to a prior art binary dye which gives a broad sensitization envelope, the dyes of the invention give much higher speed.

The invention has been described in detail with particular reference to preferred embodiments, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

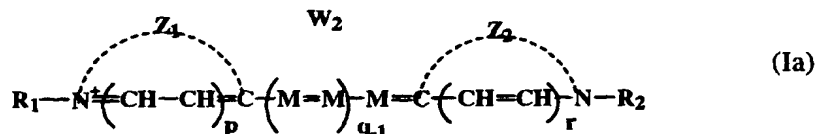
Claims

1. A silver halide photographic element comprising at least one silver halide emulsion spectrally sensitized by a molecule of formula I:



wherein Dye 1 comprises a first chromophore and Dye 2 comprises a second chromophore, wherein Dye 1 adsorbs to silver halide more strongly than Dye 2, and Dye 1 absorbs light at a longer wavelength than Dye 2, L is an organic linking group containing at least one hetero atom which is not part of an amide or ester group, and m and n are independently an integer of 1-3.

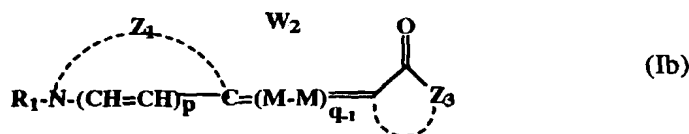
2. A silver halide photographic element according to claim 1, wherein L is an organic linking group containing at least one, preferably at least two, ether oxygen atom(s) and n and m are both 1.
3. A photographic element according to claim 1 or claim 2, wherein Dye 1 is a cyanine dye, merocyanine dye, complex cyanine dye, complex merocyanine dye, homopolar cyanine dye, or hemicyanine dye.
4. A silver halide photographic element according to claim 1, wherein Dye 1 is of formula Ia:



wherein:

Z₁ and Z₂ may be the same or different and represent the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;
each M independently represents a substituted or unsubstituted methine group,
q is a positive integer of from 1 to 4,
p and r each independently represents 0 or 1,
R₁ and R₂ each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl, and
W₂ is a counterion as necessary to balance the charge;

or of formula Ib:



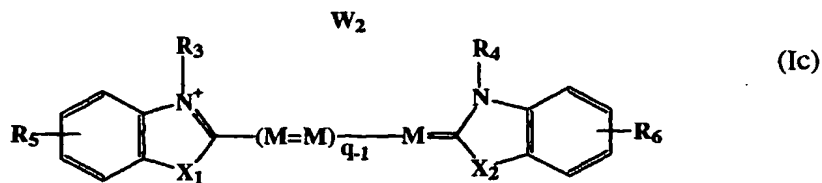
wherein:

Z₁ represents the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;
each M independently represents a substituted or unsubstituted methine group,
q is a positive integer of from 1 to 4,
p and r independently represent 0 or 1,
W₂ is a counterion as necessary to balance the charge.
R₁ and R₂ independently represent substituted or unsubstituted alkyl,
W₂ is a counterion as necessary to balance the charge, and

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Z₃ represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus;

or of formula Ic:



wherein:

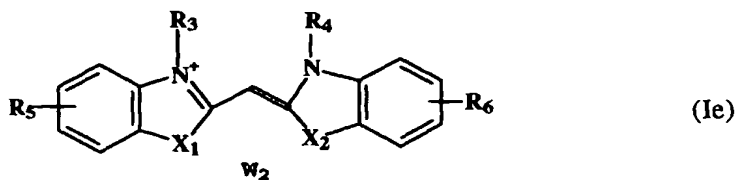
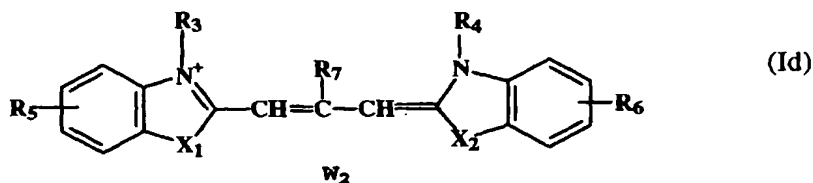
q is 1 or 2,

R₃ and R₄ each independently represents substituted or unsubstituted alkyl,

R₅ and R₆ represent one or more substituents including possible fused aromatic rings and

W₂ is a counterion as necessary to balance the charge;

or of formula Id or Ie:



wherein:

R₃ and R₄ each independently represents substituted or unsubstituted alkyl,

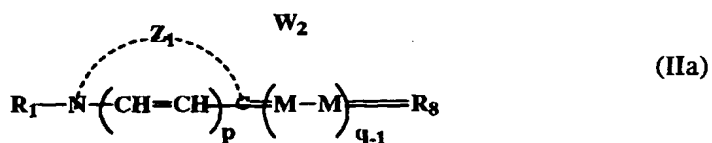
R₅ and R₆ represent one or more substituents including possible fused aromatic rings,

R₇ represents hydrogen or substituted or unsubstituted alkyl, and

W₂ is a counterion as necessary to balance the charge.

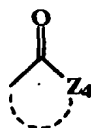
5. A silver halide photographic element according to any preceding claim, wherein Dye 2 is cyanine dye, merocyanine dye, arylidene dye, complex cyanine dye, complex merocyanine dye, homopolar cyanine dye, hemicyanine dye, styryl dye, hemioxonol dye, oxonol dye, anthraquinone dye, triphenylmethane dye, azo dye type, azomethine dye or coumarin dye.

6. A silver halide photographic element according to claim 1, wherein Dye 2 is or formula IIa:

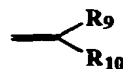


wherein:

Z_1 represents the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;
 R_1 represents substituted or unsubstituted alkyl,
 each M independently represents a substituted or unsubstituted methine group;
 p is 0 or 1;
 q is a positive integer of from 1 to 4;
 W_2 is a counterion as necessary to balance the charge; and
 R_8 represents:



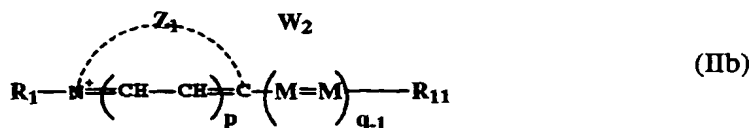
OR



wherein:

Z_4 represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus; and
 R_9 and R_{10} each independently represents a cyano group, an ester group, an acyl group, a carbamoyl group or an alkylsulfonyl group;

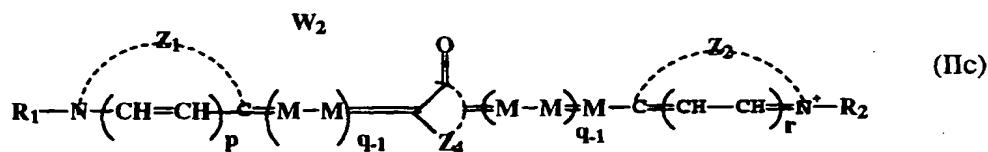
or of formula IIb:



wherein:

Z_1 represents the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;
 each M independently represents a substituted or unsubstituted methine group,
 q is a positive integer of from 1 to 4,
 p and r independently represent 0 or 1,
 W_2 is a counterion as necessary to balance the charge; and
 R_1 represents substituted or unsubstituted alkyl,
 W_2 is a counterion as necessary to balance the charge, and
 R_{11} represents a substituted or unsubstituted amino group or a substituted or unsubstituted aminoaryl group;

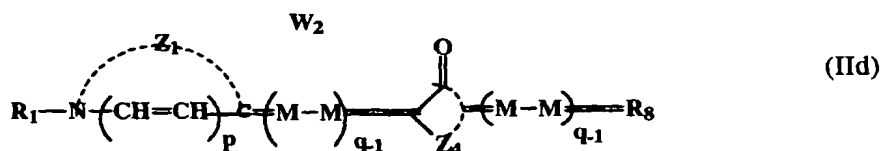
or of formula IIc:



10 wherein:

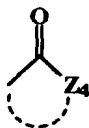
15 Z_1 and Z_2 may be the same or different and represent the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;
 each M independently represents a substituted or unsubstituted methine group,
 q is a positive integer of from 1 to 4,
 p and r each independently represents 0 or 1,
 R_1 and R_2 each independently represents substituted or unsubstituted alkyl or unsubstituted aryl, and
 W_2 is a counterion as necessary to balance the charge; and
 Z_4 represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus;

20 or of formula II d:



30 wherein:

35 Z_1 represents the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;
 R_1 represents substituted or unsubstituted alkyl,
 each M independently represents a substituted or unsubstituted methine group;
 p is 0 or 1;
 q is a positive integer of from 1 to 4;
 W_2 is a counterion as necessary to balance the charge; and
 R_8 represents: wherein:

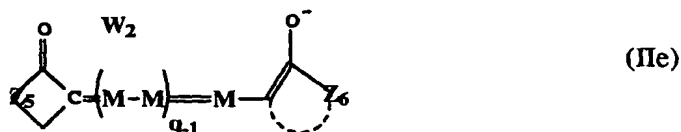


OR



50 Z_4 represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus; and
 R_9 and R_{10} each independently represents a cyano group, an ester group, an acyl group, a carbamoyl group
 or an alkylsulfonyl group;

55 or of formula II e:

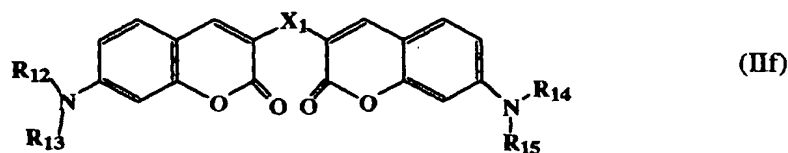


10 wherein:

each M independently represents a substituted or unsubstituted methine group;
 W_2 is a counterion as necessary to balance the charge; and
 q is 2, 3 or 4, and

15 Z_5 and Z_6 independently represent the atoms necessary to complete a substituted or unsubstituted acidic heterocyclic nucleus;

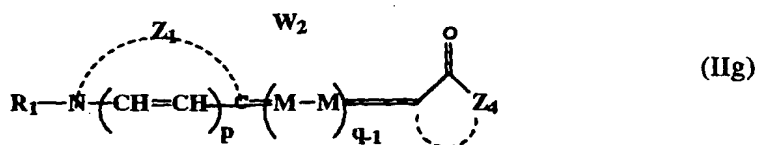
or of formula II f:



wherein:

30 X_1 represents a carbonyl group, sulfonyl group or a substituted nitrogen atom, and
 $R_{12} - R_{15}$ each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl group;

or of formula II g:



wherein:

45 Z_1 , Z_4 , R_1 , M, p, q and W_2 are as defined above for formula (II a).

Z_1 represents the atoms necessary to form a substituted or unsubstituted hetero ring which is a basic nucleus;

R_1 represents substituted or unsubstituted alkyl,

each M independently represents a substituted or unsubstituted methine group;

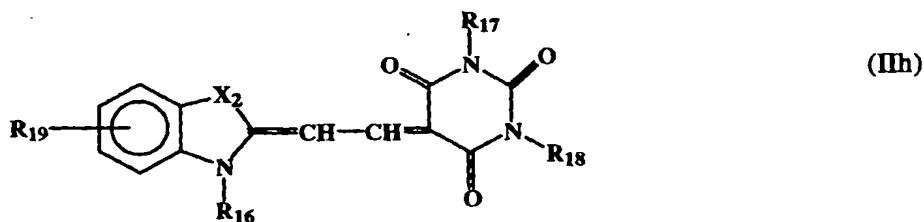
p is 0 or 1;

50 q is a positive integer of from 1 to 4;

W_2 is a counterion as necessary to balance the charge; and

Z_4 represents the atoms necessary to complete a substituted or unsubstituted heterocyclic acidic nucleus;

or of formula II h:



wherein:

X₂ is O, S, or Se,

R₁₆, R₁₇ and R₁₈ are independently substituted or unsubstituted alkyl or substituted or unsubstituted aryl, and R₁₉ represents a charged substituent or a sterically bulky substituent.

7. A silver halide photographic element according to any preceding claim 1, wherein Dye 2 does not contain a thio-carbonyl.
8. A silver halide photographic element according to any preceding claim, wherein the linking group is of the formula:

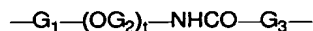


wherein each of G₁, G₂, G₃ independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups, which can have one or more intervening heteroatoms, containing 1 to 20 carbon atoms and X is a heteroatom and t is 1-8.

9. A silver halide photographic element according to claim 8, wherein the linking group is of the formula:



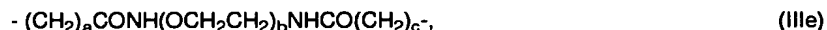
wherein each of G₁, G₂, G₃ independently represents one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene group containing 1 to 20 carbon atoms and t is 1-8; or of the formula:



wherein each of G₁, G₂, G₃ independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing 1 to 20 carbon atoms and t is 1-8; or of formula III d or III e:

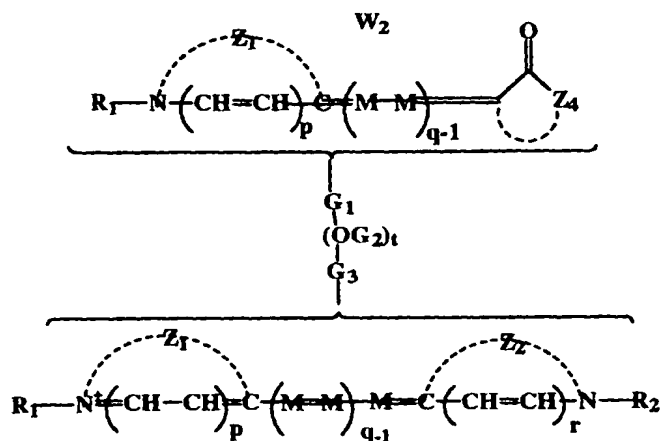


or



wherein: a, b and c are independently integers of 1 to 4.

10. A silver halide photographic element according to any preceding claim, wherein the silver halide emulsion is sensitized with a dye of formula (I) is of the structure:



25 Z_1 , Z_2 and Z_4 represent the atoms necessary to form a substituted or unsubstituted hetero ring and may be the same or different,

each M independently represents a substituted or unsubstituted methine group,

q is a positive integer of from 1 to 4,

p and r each independently represents 0 or 1,

s is a positive integer of from 2 to 4,

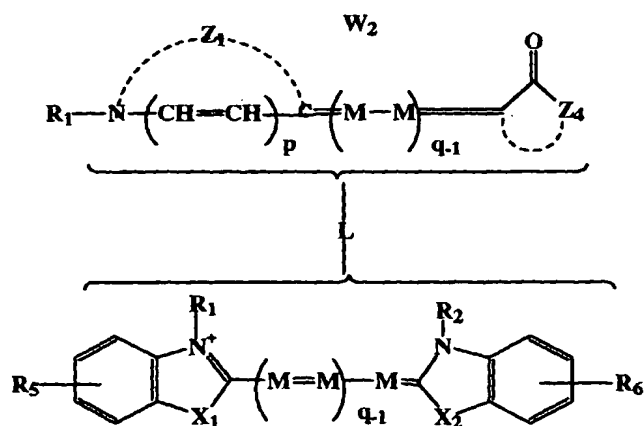
R_1 and R_2 each independently represents substituted or unsubstituted alkyl or unsubstituted aryl, and

30 W_2 is a counterion as necessary to balance the charge;

wherein each of G_1 , G_2 and G_3 independently represent one or more substituted or unsubstituted alkylene or substituted or unsubstituted alkenylene groups containing 1 to 20 carbon atoms

t is a positive integer of from 1 to 6;

35 or of the structure:



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each M independently represents a substituted or unsubstituted methine group,

q is a positive integer of from 1 to 4,

p represents a positive integer 0 or 1,

R₁, R₂ and R₃ each independently represents substituted or unsubstituted alkyl or substituted or unsubstituted aryl,

R₅ and R₆ each represent one or more substituents including possible fused aromatic rings, and

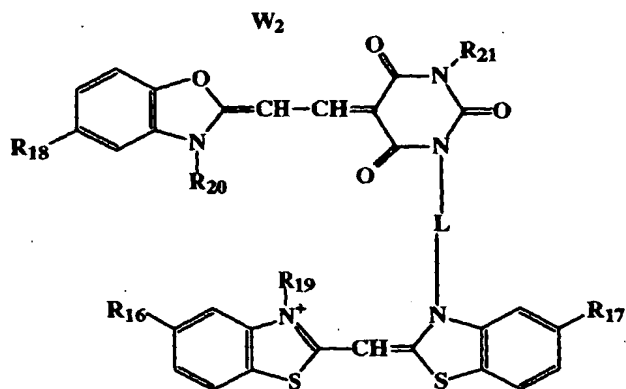
W₂ is a counterion as necessary to balance the charge;

L represents



and each of G₁, G₂, G₃ independently represent one or more substituted or unsubstituted alkylene or methine groups containing 1 to 20 carbon atoms and t is a positive integer of from 1 to 6;

or of the structure:



wherein:

R₁₆ and R₁₇ are independently halogen, substituted or unsubstituted alkyl, substituted or unsubstituted aryl, a fused aromatic ring, or a heteroaryl group,

R₁₉ is substituted or unsubstituted alkyl or substituted or unsubstituted aryl group,

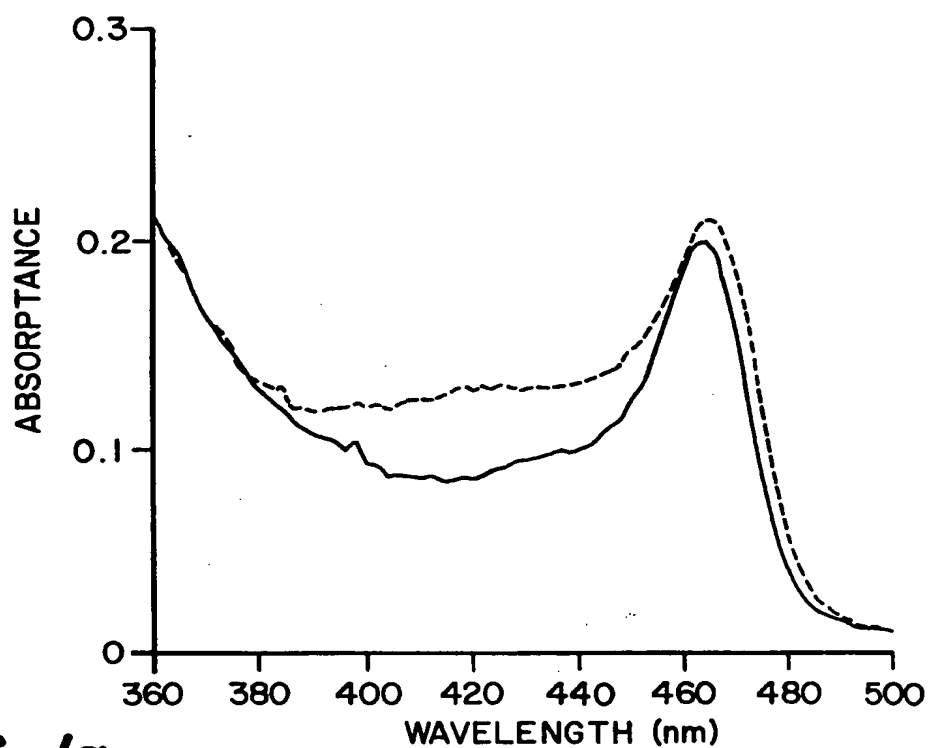
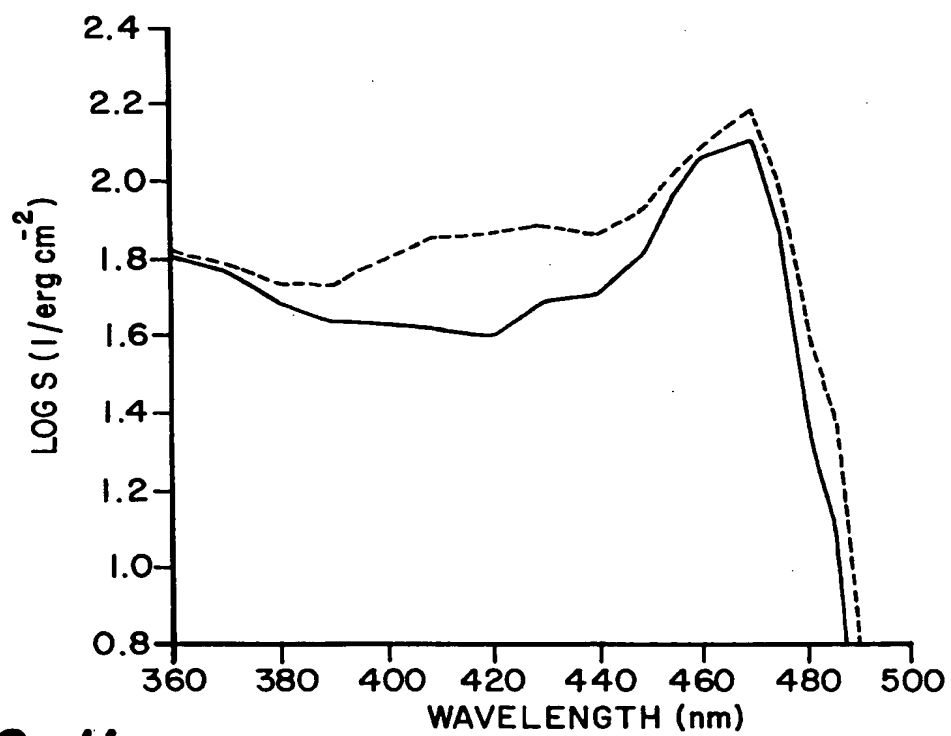
R₁₈ is a substituted or unsubstituted alkyl group,

R₂₀ is a substituted or unsubstituted alkyl group and

R₂₁ is a hydrogen atom or a substituted or unsubstituted alkyl or substituted or unsubstituted aryl group,

W₂ is a counterion as necessary to balance the charge;

-L- is of the structure $-(CH_2)_a(OCH_2CH_2)_bNHCO(CH_2)_c-$, wherein: a, b and c are independently integers of 1 to 4.

**FIG. 1a****FIG. 1b**



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 1969

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	FR 930 514 A (GEVAERT) 3 February 1948 * page 1, line 8 - page 2, line 16; claim *	1-9 10	G03C1/12
D,A	JP 01 091134 A (FUJI) 10 April 1989 * page 2, left-hand column, line 33 - page 6, left-hand column, line 1 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 September 1998	Examiner Magrizos, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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